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ELECTROMAGNETIC MERCURY PUMPS FOR CIRCULATING GASES¹

BY I. E. PUDDINGTON

Abstract

Designs for two gas circulating pumps are described. In one of these, bulbs are attached to each end of a U tube, and mercury is made to flow alternately from one bulb to the other through the U thus forming a liquid piston. This may be used either as a double or single action pump. In the second design, which is also a modified U tube, the mercury is circulated continuously in one direction. Gas is entrained between slugs of mercury as it flows externally from one arm of the U to the other to complete the cycle. Circulation speeds of 600 to 800 cc. of gas per minute can readily be obtained with either of these models. In both designs the mercury is pumped electromagnetically. The small space requirements and the absence of mechanically moving parts are desirable properties of these pumps.

Positive circulation of gas in sealed glass systems is frequently required in experimental physical chemistry. At low pressures mercury diffusion pumps are quite satisfactory for this purpose. If, however, the gas pressure exceeds a few mm. other means of inducing circulation must be found. While various pump designs have appeared in the literature, these usually possess such shortcomings as large space requirements, mechanically moving parts, lack of indication of pumping rates, or volume change during operation, and cannot therefore be considered ideal. Electromagnetic pumping of molten metals has been used industrially (1) and, since the application of this principle to gas circulating pumps using mercury would appear to eliminate many of the objections listed above, the following designs are suggested:

One form of electromagnetic pump is similar in principle to a d-c. electric motor in which the armature is replaced by a molten metal, in this case mercury. Flow of the mercury is produced by passing an electric current through it at right angles to a magnetic field. Since the effective number of turns of conductor in the magnetic field that can be used is limited, low voltages and rather high currents are required to transfer useful volumes of liquid. The pressure that can be developed in this way from a single turn can be calculated

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa,
Ontario. Issued as N.R.C. No. 2448.*

from the formula:

$$P = \frac{10^{-3} BI}{W}$$
 where B = kilogauss
 I = amperes
 W = width of mercury path in mm.
 in direction of magnetic field
 P = atmospheres

In early experiments attempts were made to use a shaded pole a-c. stirring motor by removing the armature and inserting a multturn helix, filled with mercury, into the cavity surrounded by the field coils. This did not produce a sufficient head to be useful, although this situation might be improved with suitable iron cores.

Two successful models using the d-c. principle are shown in Figs. 1 and 2. In both of these designs a permanent alnico magnet having a field strength of about 4000 gauss, with the pole pieces in place, was used. The poles of this

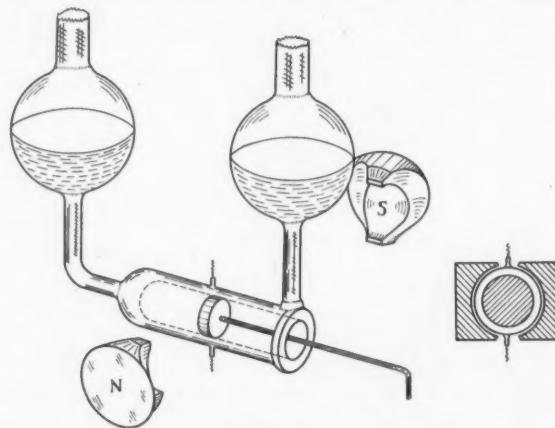


FIG. 1.

magnet were circular, with a diameter of 1.5 in. and were spaced 1.5 in. apart. The pole pieces were made of cold rolled steel and were shaped approximately as shown in the figures.

The apparatus shown in Fig. 1 uses a single pass system and operates at a low head. A high pumping speed is effected by using a long current path and a short magnetic gap. This was accomplished by sealing a glass tube of 25 mm. o.d., inside another of 26 mm. i.d., to produce an annular space about 0.5 mm. wide. Platinum electrodes in the top and bottom allowed the electric current to follow both paths from top to bottom through the mercury filled annulus. A core of mild steel rod about 5 mm. long and 22 mm. in diameter gave a short magnetic gap and produced radial lines of force through the annulus.

The current from a single No. 6 dry cell (about 10 amp.) produced a height differential of about 3 cm. in the mercury contained in vertical tubes attached

to either end of the annular space. Thus by reversing the current a total pressure change of 6 cm. could be realized. In the model shown in Fig. 1, a 200 cc. round bottom flask was attached to each side of the pump and mercury was added until these flasks were about half full. By reversing the current at appropriate intervals the flasks could be made to fill and empty alternately

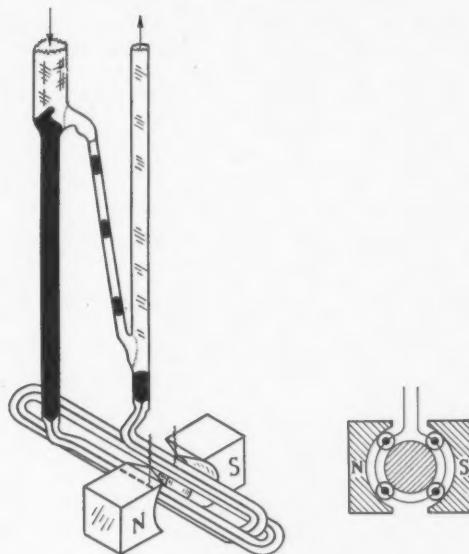


FIG. 2.

with mercury. This arrangement was made to operate automatically by using a modified mechanical latch relay as a double pole, double throw switch set to reverse the current through the annulus when the mercury made contact with electrodes set at appropriate heights in the bulbs.

In this set up the pumping speed is obviously greater if the direction of flow of the current is reversed before the mercury reaches its maximum possible level, and a short cylinder might be a better shape for the reservoirs than the spheres used here.

Using currents of 10 to 12 amperes, equivalent gas circulating speeds of the order of 800 cc. per minute were obtained if the device is considered as a double acting pump. This, of course, requires the use of external valves not shown here. If it is desired to avoid valves a single action pump having an arrangement similar to one already described (2) can be used. It would appear to be quite feasible to use much higher currents (20 to 30 amp.) should higher pumping speeds be required. The power used in the pumping is small; the potential drop across the pump was about 0.2 volt for a current of 10 amp. The mercury showed virtually no heating after several hours of operation.

In the second design of this type of pump a multipass system of the mercury through the magnetic field was used, thus increasing the head to which it can be pumped although greatly reducing the through-put. The tubes pass through the field in such a way that an annulus of tubes is formed. The ends of these tubes are connected to make the mercury flow in one direction on one side of the annulus and in the reverse direction on the other side. This is shown in Fig. 2 where four passes only are shown for simplicity. The electrodes were No. 20 platinum wire and the current flows around the annular space.

In this model, 1 mm. pyrex capillary was used to give mechanical strength. This, however, limited the number of passes that could be made through the magnetic field to 8, using the pole pieces already described. With this arrangement, the head obtained was approximately proportional to the number of passes, and a head of 30 cm. was produced with a current of 17 amp. Circulation of the gas was accomplished in this case by allowing the mercury to fall in slugs down the section of 4 mm. i.d. tubing used to connect the two vertical limbs of the apparatus. With the current of 17 amps. a potential drop of 0.5 volt occurred at the platinum leads, and mercury at the rate of three slugs per second passed through the connecting tube. With no backing pressure each slug had ample time to fall completely through the 24 cm. tube before a new one appeared at the top. This caused gas circulation at the rate of about 600 cc. per minute. Appreciable backing pressure such as the insertion of a cork stopper in the outlet tube materially reduced this rate, however.

The 1 mm. diameter tubing used to carry the mercury through the magnetic field seemed to be the most suitable to give a high head. It produced a gap of about 1 mm.² in cross section at the electrodes. The wall thickness of this tubing, however, is probably excessive and it should be possible with the use of less wall thickness to produce a higher magnetic flux density as well as increase the number of passes, should higher heads be required. Heads up to one atmosphere should be obtainable without too much difficulty.

The procedure used to assemble these multiple pass systems was simple: Electrodes were sealed into pieces of capillary about 10 cm. long. These were then fitted around a 5/8 in. metal bar, held in place with rubber bands and metal spacers until the individual tubes could be tacked together with a bridge of glass. Following this the ends were appropriately connected using capillary U-shaped connectors. The adjacent ends of the platinum electrodes were then soldered together. This procedure ensured the easy insertion of a neat fitting mild steel core.

A d-c. electromagnet connected in series with the current through the mercury was successfully used with both of these models. While the particular electromagnet available did not possess a laminated core and was sufficiently inductive to pass only five amperes at 220 volts, the pumping was quite visible, and it seems probable that suitable a-c. designs could be developed.

A variation of this multipass system is shown in Fig. 3. Here the pyrex capillary is bent in the form of a flat rectangular coil. This produces two groups of mercury conductors one directly above the other. Leads for the electric current are arranged in a vertical line and four triangular, prism-shaped pole pieces are arranged, one on each side of the electric conductors. The dis-

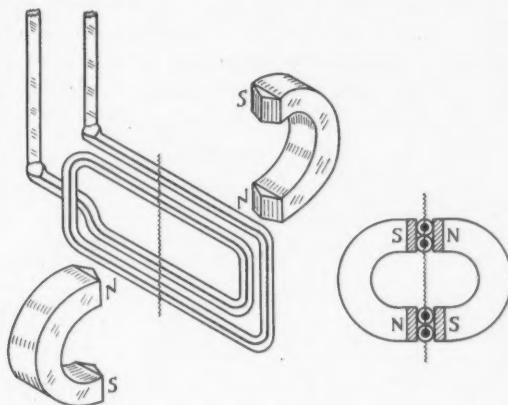


FIG. 3.

tance between the two groups of capillaries is arranged to be approximately the same as the distance between the poles of available horseshoe magnets. Field strength can be adjusted to give the desired flux by the addition of extra magnets using the common pole pieces. A group of magnets is then placed on each side of the electric conductors. The number of passes of the mercury con-

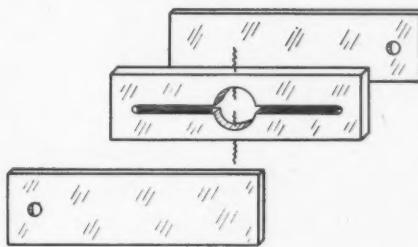


FIG. 4.

ductors can be arranged to give complete coverage of the available pole piece area. With this arrangement heads of 20 cm. were obtained, using 10 amperes current and two groups of three alnico horseshoe magnets ($1\frac{7}{8} \times 1\frac{3}{4} \times \frac{3}{4}$ in.) and eight passes of the mercury.

Partial success was obtained with a multipass system using sheet cellulose acetate 0.015 in. in thickness to hold the electrodes and form the mercury

passage. These were spaced with cellulose acetate separators 0.005 in. in thickness. This arrangement gave about 10 passes in a space 0.25 in. thick. One unit of the assembly is shown in an "exploded" view in Fig. 4. The chief difficulty encountered with this model was obtaining a seal between the cellulose acetate and platinum, and cellulose acetate and the glass side arms, sufficiently tight to prevent leakage of the mercury when the pressure built up. Any local heating also tended to produce a bubble of vapor which interrupted the electric current as it passed between the electrodes, and since a series arrangement is used, this stopped the mercury flow. In view of these difficulties attempts to use plastics were abandoned in favor of the all-glass models.

Designs other than those suggested would probably be equally useful. However, these serve to illustrate a useful application of electromagnetism that heretofore seems to have received little attention.

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ESTIMATION OF GLYCOGEN BY THE USE OF ANTHRONE¹

BY RUTH PETERSON AND DYSON ROSE

Abstract

A method for estimating glycogen in rat and pork liver and muscle is described. Interfering substances that react with anthrone to produce brown discolorations are eliminated by a preliminary adjustment of the pH to 4.0 and centrifugation. Glycogen is then precipitated from an aliquot of the supernatant by adding ethanol; the precipitate is redissolved in water, and reacted with anthrone. The satisfactory range of the method is from 20 to 350 μgm . per colorimeter tube. A set of eight determinations can easily be made in a working day, and the accuracy of the method is equal to that of the hydrolysis-reducing sugar methods.

Introduction

Most methods for estimating glycogen involve digestion, partial purification, hydrolysis, and determination of the reducing sugar formed. Seifter *et al.* (8) have published a method for determining glycogen without hydrolysis by using the anthrone reagent, and have shown that this method equals the reducing sugar method in accuracy. These authors state that interference due to residual tissue constituents is negligible except at low glycogen levels, but in our experience the brown discolorations previously noted by Dreywood (2) seriously interfered with determinations of glycogen in rat and hog livers. Seifter *et al.* attempted to precipitate the proteinaceous materials with several reagents including trichloroacetic acid but did not consider the results satisfactory. The present paper describes a simple method for eliminating most of the interfering materials before precipitation of the glycogen.

Recommended Method

Reagents

Potassium hydroxide, 30% w/w.

Methyl red indicator solution.

Hydrochloric acid, at approximately 1 N and 0.1 N strengths.

Ethanol, 95% and 66%.

Crystalline anthrone prepared by the method of Meyer as summarized by Morris (7). A 0.1% solution in concentrated sulphuric acid is prepared and stored in a dark bottle for at least four hours but not more than nine days (9).

Glycogen (Eastman Kodak), a stock solution containing 1 mgm. per ml. is diluted 1: 25 for use.

¹ Manuscript received March 14, 1951.

Contribution from the Division of Applied Biology, National Research Council, Ottawa, Canada. Issued as Paper No. 264 of the Canadian Committee on Food Preservation and as N.R.C. No. 2445.

Procedure

Weigh approximately 2 gm. of tissue accurately in a small beaker. Add 2 ml. of 30% potassium hydroxide for each gram of tissue present, then heat the mixture on a steam bath for 45 min. or until free from undissolved lumps. Transfer this solution to a volumetric flask of suitable size and make to volume. For samples that are relatively high in glycogen a 100 ml. flask is preferable; for samples low in glycogen a 50 ml. flask should be used.

Pipette 5 ml. of this digest into a 25 ml. volumetric flask and acidify with 1 N hydrochloric acid to the first color change of methyl red and then adjust to the flocculation point (pH 4.0) with 0.1 N acid. Make the solution to volume, allow to stand for two or three minutes, and centrifuge a portion for 10 min. at 1800 r.p.m. Decant the supernatant and discard the precipitate.

Pipette a 3 ml. aliquot of the supernatant into a 15 ml. centrifuge tube and add 6 ml. of 95% ethanol. Mix the contents of the tube with a stirring rod and rinse down the rod and the walls of the tube with 66% ethanol.

Additional 66% ethanol may be used to balance the tubes for centrifuging. Centrifuge at 1800 r.p.m. for 25 min. and discard the supernatant immediately. Dissolve the precipitate in a few ml. of distilled water and transfer to a 10 or 25 ml. volumetric flask. Make to volume with distilled water.

Pipette 5 ml. of this solution into a standard colorimeter tube. Add 10 ml. of anthrone reagent from a carefully selected pipette that will deliver the reagent in 20 to 25 sec., swirling the tube uniformly but vigorously during this addition. Allow the tubes to cool in air for 20 to 30 min. and then read the color density at 5400 Å against a blank containing 5 ml. of water and the anthrone reagent.

Along with the samples prepare a standard containing 5 ml. of diluted glycogen solution (200 µgm. of glycogen). Plot the per cent transmission of the standard on semilog paper and draw the standard curve as a straight line connecting this point with zero. Read off the glycogen content of the sample.

The range of the method is approximately 10 to 140 mgm. per gm. of tissue at original and final volume of 100 and 25 respectively, and 2 to 30 mgm. per gm. at 50 and 10. The lower limit can be still further reduced by taking a larger aliquot for acidification (with concentrated hydrochloric acid to avoid exceeding the 25 ml. volume) and by using an aliquot of 4 ml. with 8 ml. of ethanol for precipitation of the glycogen. For acceptable results there should be at least 20 µgm. of glycogen in the 5 ml. aliquot taken for color formation.

Experimental

Precipitation of Interfering Materials

The digestion and glycogen precipitation steps included in this method have been adapted from published methods (3, 5, 10). However, in these methods the digest was neutralized in the presence of alcohol so that both glycogen and

various proteose materials were precipitated at once. The latter was subsequently destroyed during acid hydrolysis of the glycogen and therefore did not interfere with the copper reduction procedures. Use of anthrone eliminates the hydrolysis step and, in our experience, the proteose materials then interfere seriously. It was therefore necessary to divide the precipitation step into two phases.

Precipitation of the proteoses is accomplished by adjusting the pH in the absence of alcohol. Accurate adjustment of the pH is required to obtain good flocculation; a somewhat colloidal suspension forms if the solution is more acid than pH 4.0. Table I presents the results of analyses made on aliquots of the

TABLE I
EFFECT OF pH ON RECOVERY OF GLYCOGEN FROM PORK MUSCLE DIGEST
(Glycogen added, 20 mgm.; single determinations)

| pH for precipitation | Glycogen recovered | |
|----------------------|--------------------|-------|
| | Mgm. | % |
| 4.04 | 20.3 | 101.5 |
| 5.08 | 21.2 | 106.0 |
| 5.99 | 25.8 | 129.0 |
| 6.98 | 25.8 | 129.0 |

same glycogen free (pork muscle) digest adjusted to various pH levels. The data indicate that interference due to tissue constituents is almost completely eliminated at pH 4.0. With practice this adjustment can be readily made with methyl red indicator but checking the pH with a meter is recommended until the analyst becomes familiar with the procedure. After pH adjustment the mixture should be allowed to stand for two or three minutes to complete the flocculation and improve the centrifugal separation. Filtration through paper is undesirable as cellulose fiber may be left in the solution. Excessive delay must be avoided during this stage as glycogen is hydrolyzed in acid solution.

Table II presents the results of recovery experiments in which known amounts of glycogen were added to digests of rat liver and muscle before the pH was adjusted. These data indicate that recovery of glycogen is satisfactory under these conditions although the results tended to be somewhat high with the muscle digests.

Precipitation of Glycogen

As the supernatant from the above step is acid, glycogen is precipitated immediately upon the addition of alcohol. The strength of alcohol used is that recommended by Grattan and Jensen (4). Separation of the fine precipitate of glycogen is satisfactorily accomplished by 25 min. centrifugation at 1800 r.p.m. Higher speeds could not be used with glass tubes, and plastic tubes led to contamination of the glycogen. The alcoholic supernatant had to be de-

canted as quickly as possible after centrifugation as the precipitate tended to dislodge from the bottom of the tube if allowed to stand. Re-solution of the glycogen presented no difficulty even when small amounts of alcohol remained in the tube.

TABLE II
RECOVERY OF GLYCOGEN ADDED TO LIVER AND MUSCLE DIGESTS
BEFORE PRECIPITATION OF THE PROTEOSE MATERIAL
(Averages of duplicate determinations)

| Sample | Glycogen content, mgm./gm. | Glycogen added, mgm./flask | Glycogen found, mgm./flask | Recovery, % |
|--------|----------------------------|----------------------------|----------------------------|-------------|
| Liver | 32.43 | 5 | 5.13 | 102.6 |
| Liver | 30.95 | 5 | 4.96 | 99.2 |
| Muscle | 3.83 | 3 | 3.17 | 105.7 |
| Muscle | 3.30 | 3 | 3.13 | 104.3 |

Color Development

The degree of heating that occurs during addition of anthrone reagent to the sample influences the final color density, but this can be controlled by using standard tubes and a selected pipette. Alternately the use of a cooling bath followed by 10 min. heating as recommended by Seifter *et al.* (8) and by Long (6) may be used, although this technique has been questioned by Barnett *et al.* (1).

Maximum light absorption by the colored solution occurs at 6200 Å (8, 9), but the range of the method is extended by reading the color density at 5400 Å (7, 9). In our experience the variability of the results was reduced when the color was read at 5400 Å and, after elimination of the interfering substance that gave rise to a brownish color, this wave length appeared to be most satisfactory.

The value obtained with the standard glycogen solution did not vary more than two galvanometer units during the recommended life (9) of the anthrone reagent: With the Evelyn instrument the galvanometer reading for 200 µgm. of glycogen per tube averaged 35.8 for a series of 61 readings, over a 15 month period.

Discussion

Although the lower limit of the range of this method is somewhat high, we feel that its accuracy is sufficiently greater than that of the more direct anthrone methods to justify its use. In tissues of very low glycogen content recourse must be had to methods with fewer dilution steps. Applicability of the method to other tissues has not been tested, other than a few determinations on mouse liver, which indicated that flocculation of the proteoses occurred at a slightly lower pH than with rat liver but could be successfully accomplished.

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A STUDY OF MASS TRANSFER RATES FROM THE SOLID TO THE GAS PHASE¹

BY A. C. PLEWES AND J. KLASSEN

Abstract

Five pure solids have been vaporized in turbulent air streams, and the results indicate that the evaporation processes may be correlated by the Sherwood-Gilliland relationship for the vaporization of liquids from moving films into turbulent air streams:

$$\frac{d'}{x} = 0.023 Re^{0.83} Sc^{0.44}$$

This work indicates that the mechanism for mass transfer in gas-solid systems is analogous to that existing for liquid-gas systems. The results also offer a convenient method of estimating rates of sublimation and condensation in solid-gas systems.

Introduction

The transfer of material from one phase to another is an essential feature of many widely used unit operations in the field of chemical engineering. Included in this group are absorption, extraction, distillation, and crystallization. The adsorption of gases and heterogeneous gas reactions on solid surfaces involve quite similar phenomena. In order to design equipment to carry out the above operations, the chemical engineer must have reliable data on the rate of this material transfer under conditions prevailing in the equipment in actual service. Much research on this problem has been done, but different investigators (1, 3, 6, 9, 11, 14) have presented results which differ, in some cases appreciably and in others only slightly, from each other. The data are usually expressed by equations based on the various resistances offered to mass transfer where the total resistance for a heterogeneous system is considered to be made up of individual resistances in each of the phases concerned.

Whitman's two-film theory (15) is generally employed in correlating experimental results. It is postulated that at the interface between phases equilibrium exists or, in other words, that no resistance to mass transfer is offered by the interface itself. It is further supposed that adjacent to the boundary between phases there is a stagnant film of material, regardless of the turbulence of the main body of the fluid, which is considered to offer the total resistance to mass transfer. While this theory neglects turbulent or eddy diffusion in the main bulk or core of the fluid stream, the simplified correlation is successful because this variable does not change very much from one system to another.

The transfer of material across fluid films is treated quantitatively as true diffusion of one component through a second stagnant component which con-

¹ Manuscript received January 16, 1951.

Contribution from the Department of Chemical Engineering, Queen's University, Kingston, Ontario.

stitutes the fluid film. The basis of the mechanism for gases is a part of the kinetic theory which was developed principally by Maxwell (8) and Stefan (12, 13), and the results of this theory may be expressed as follows:

$$N_A = \frac{DP\Delta p_A^*}{RTx\bar{p}_{BM}}. \quad (1)$$

It now remains to determine the relationship between the parameters describing the equipment and the flow of fluids in actual cases to the gas film properties. The most general correlations are based on dimensional analysis. The variables are combined into dimensionless groups with exponents which are determined experimentally. The most important work involving mass transfer in vapor films was first done by Sherwood and Gilliland (5) in a wetted-wall column of circular cross section and has since gained wide acceptance. Their data were correlated by means of the dimensionless equation:

$$\frac{d}{x} = 0.023 Re^{0.83} Sc^{0.44}. \quad (2)$$

Other workers (1, 3, 6, 9, 11, 14) have proposed equations of the same general form but with different numerical constants. In their work the numerical factor is as high as 0.5, the exponent of the Reynolds number falls between 0.8 and 0.6, and the exponent of the Schmidt number is 0.33. In addition, work on individual film resistances in packed towers for absorption and rectification processes (2) indicates that a more thorough study must be made of the vapor resistance before a clearer understanding of diffusion in packed systems can become possible.

It is obvious, however, that the mass transfer problems involved in packed towers will be more complex than the simpler diffusional process used by Gilliland. In the latter case, a study was made of vaporization of pure liquids into turbulent air streams from a liquid film in a wetted-wall tower. The velocity of the liquid constituting the film was maintained at a constant value in the laminar flow region, and it was thought that under these circumstances the liquid phase resistance was negligible and that the overall resistance to mass transfer was due to the vapor phase resistance.

It was believed that the presence of the liquid phase might have produced inconsistencies that could account for the erratic results observed by former workers (1, 3, 6, 9, 11, 14). If the liquid film could be physically excluded from the system, at least one unknown variable could be eliminated. It was planned, therefore, to examine mass transfer processes by investigating solid-vapor systems.

Experimental

The apparatus consisted essentially of a unit in which a measured air stream contacted a liquid or solid surface at a known temperature. Fig. 1 shows the apparatus in diagrammatic form.

* The symbols used in this and subsequent equations are defined at the end of the paper under the heading of 'Notation'.

The air stream was created by a fan of 125 c.f.m. maximum capacity, and controlled by a system of dampers. From the fan the air was led over finned refrigerator coils which removed most of the moisture from the air by cooling the gas to an average temperature of -10°C . The cooled air then passed over nichrome wire heating coils which were of such capacity that they could raise the temperature of the air by 40°C . at the maximum flow rate. The current through the coils was measured by an ammeter and regulated by rheostats. The air duct immediately beyond the heaters was reduced in size from $7\frac{1}{2}$ in. diameter copper tubing to square, 2 in. steel piping. This marked the entrance to the calming section. The air after reaching the contraction passed through the calming section and around the head of a Pitot meter which was used in conjunction with an oil manometer on which liquid levels could be read to 0.005 mm. The air then passed through another calming section and over

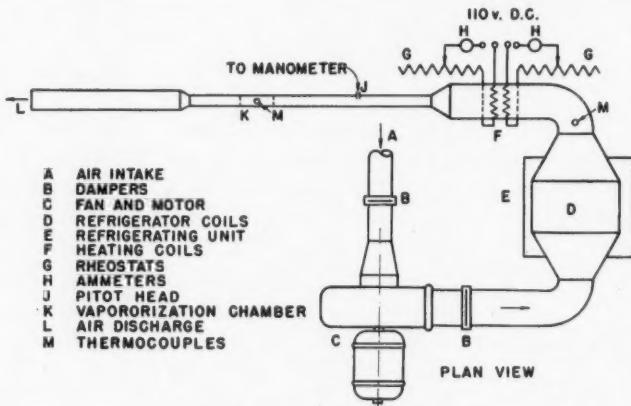


FIG. 1. Sketch of the apparatus.

the surface of the evaporating solid before it was discharged to the outside atmosphere. A system of baffles was placed around the air intake and discharge lines so that any wind fluctuations in the outside atmosphere would not appreciably affect the flow rate in the apparatus. All air ducts in the unit were covered with asbestos paper insulation to minimize heat transfer to and from the ambient atmosphere. This enabled wider variations in the temperature, both above and below that of the room air, to be maintained.

Temperatures within the systems were measured with copper-constantan thermocouples and a self-balancing potentiometer. The air stream temperature in the vaporization chamber was measured and taken as the temperature at which vaporization occurred. To test this assumption a trial run was conducted with a thermocouple embedded in the solid just below the surface. The temperature of the solid near the phase interface did not differ from the air temperature by more than 1.0°C . Thermocouples rather than thermometers were used because the former caused less disturbance of the streamlines in the air stream.

The vaporization chamber was 5.23 cm. square in cross section and was so designed that irregularities in the air flow due to obstructions were minimized. The chamber and the calming sections were identical in cross section. The calming sections before and after the vaporization chamber were straight lengths of pipe 29 and 18 diameters long respectively. Subsequent work on equipment with longer calming sections has given results similar to those reported here. A rectangular opening was cut in the bottom of the chamber through which the solid was exposed to the air stream. The depth of the pan which contained the solid was equal to the thickness of the pipe which formed the vaporization chamber so that the surface of the solid was flush with the surface of the air duct. This arrangement, which ensured that no obstruction or change in shape existed in front of or behind the vaporizing surface, is shown in Fig. 2.

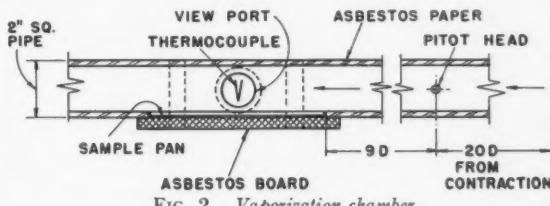


FIG. 2. Vaporization chamber.

The sample pan exposed an evaporating surface of 3.8 by 20.7 cm. It was held in place by sheet metal straps which passed around outside of the chamber. Another feature of the positioning arrangement was a 1/2 in. asbestos board placed over the bottom of the pan surface which would otherwise have been in direct contact with the atmosphere. Heat transfer between the sample and surroundings and the ensuing occurrence of temperature gradients within the vaporizing material were thus prevented. This was especially important at temperatures differing appreciably from room temperature. The vaporization chamber was also provided with a lucite viewing port so that the surface of the substance under study could be observed during evaporation. This was especially helpful when liquids were being studied because undue splashing and spilling were immediately detected.

The rate of evaporation was measured by weighing the solid and pan before and after a run and recording the duration of the run with a stop watch. For the more volatile substances, vaporization occurred so rapidly that corrections in the weighings had to be made. Daily measurements of the rate of evaporation of these materials on the balance pan were carried out. The times required for weighing the solid and pan before and after the run were noted and a correction was applied to the loss in weight.

Results

The original study of this problem involved the vaporization of liquid benzene. It was believed that if the motion of the liquid played a role in evap-

oration this phenomenon could be minimized by the use of a stationary liquid film. The data are given in Table I and shown graphically in Fig. 3. A sample calculation is given by Sherwood and Gilliland (5). These workers in their

TABLE I
VAPORIZATION OF LIQUID BENZENE AT 15°C.

| Temp., °C. | Pressure, mm. Hg | Air rate, cc./sec. | $N_A \times 10^6$, gm-mol. sq. cm. sec. | Re | d/x | $\frac{d'}{x}$ $\text{Sc}^{0.44}$ |
|------------|------------------|--------------------|---|--------|------|--------------------------------------|
| 14.0 | 753 | 26,400 | 1.21 | 39,500 | 274 | 210 |
| 14.1 | 753 | 26,300 | 1.19 | 39,300 | 269 | 206 |
| 14.0 | 753 | 25,900 | 1.01 | 38,700 | 228 | 175 |
| 17.5 | 753 | 22,000 | 0.864 | 32,400 | 172 | 130 |
| 16.8 | 753 | 22,000 | 0.774 | 32,300 | 146 | 112 |
| 17.8 | 753 | 21,800 | 0.786 | 32,100 | 148 | 114 |
| 17.0 | 753 | 11,300 | 0.450 | 16,700 | 89.1 | 68.2 |
| 17.2 | 753 | 11,200 | 0.415 | 16,500 | 80.8 | 61.8 |
| 16.7 | 753 | 11,200 | 0.439 | 16,500 | 84.8 | 65.0 |
| 15.5 | 753 | 9080 | 0.409 | 13,400 | 86.5 | 66.2 |
| 15.5 | 753 | 9060 | 0.360 | 13,400 | 75.8 | 58.0 |
| 15.5 | 753 | 9010 | 0.330 | 13,400 | 69.5 | 53.3 |
| 16.7 | 753 | 5460 | 0.258 | 8070 | 51.0 | 39.1 |
| 16.5 | 753 | 5430 | 0.258 | 8020 | 51.6 | 39.5 |
| 15.9 | 753 | 5380 | 0.266 | 7970 | 54.8 | 39.7 |

research used a wetted-wall column which was circular in cross section. In correlating their results they used the column diameter as d . Rouse (10) shows that for noncircular cross sections four times a quantity termed the hydraulic

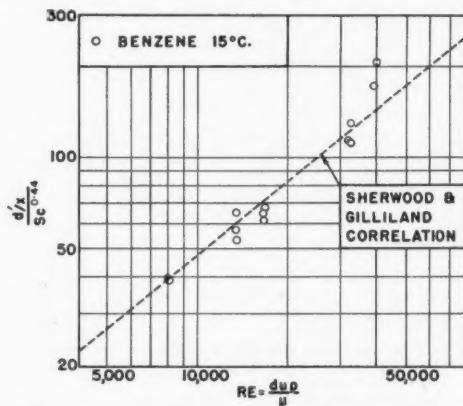


FIG. 3. Mass transfer from the liquid to the gas phase.

radius should be used. This radius is given by the cross sectional area divided by the perimeter of this area. In the apparatus used here the vaporization chamber was 5.23 cm. square. The value of four times the hydraulic radius in this case is simply the side of the square, 5.23 cm. In calculating the Reynolds number this value is used for d .

The equivalent diameter in the ratio d'/x is characteristic of diffusional conditions and its value is based on the cross sectional area and perimeter of the surface of the solid which evaporated. For this work d' amounts to 6.2 cm.

Values of the diffusion coefficient are calculated by the empirical equation proposed by Gilliland (4).

It will be observed that when the Reynolds number is plotted against the ratio $\frac{d'}{x} / Sc^{0.44}$ on logarithmic coordinates the experimental data follow the Sherwood-Gilliland equation up to a Reynolds number of 30,000. Beyond this point it is difficult to obtain consistent and reliable data. The reason for this latter behavior was evident on examination of the liquid surface through the lucite window located in the side of the vaporization chamber. It was noted that at high Reynolds numbers the rapid motion of the air past the liquid surface produced a wave motion in the liquid and in some cases tore small liquid droplets away from the surface. This action undoubtedly increased the

value of $\frac{d'}{x} / Sc^{0.44}$. This would explain the position of the two points at Reynolds numbers above 30,000 in Fig. 3. It must be stated that these points were not the results of only two experiments but of many repeated determinations. These data indicate that the Sherwood-Gilliland equation cannot be used unless the liquid film exists in the undisturbed state. Such a condition is possible if the Reynolds number for the moving fluid is low enough to result in laminar flow.

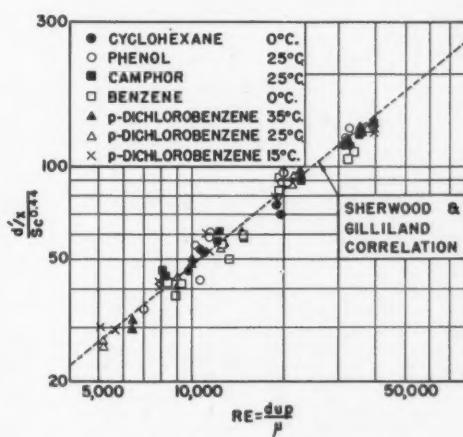


FIG. 4. Mass transfer from the solid to the gas phase.

The second phase of the work was carried out by vaporizing pure solids. It will be noted from Fig. 4 and Tables II to VIII that such compounds as benzene, cyclohexane, phenol, camphor, and *p*-dichlorobenzene were studied.

TABLE II
VAPORIZATION OF SOLID BENZENE AT 0°C.

| Temp. | Pressure | Air rate | $N_A \times 10^5$ | Re | d/x | $\frac{d/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|-------------------------|
| 1.0 | 768 | 20,200 | 0.290 | 33,200 | 149 | 114 |
| 1.0 | 763 | 20,000 | 0.290 | 32,900 | 148 | 114 |
| 1.0 | 763 | 19,400 | 0.277 | 31,800 | 142 | 108 |
| 3.0 | 768 | 12,000 | 0.280 | 19,500 | 124 | 95.4 |
| 3.0 | 760 | 11,800 | 0.277 | 19,300 | 123 | 94.0 |
| 1.0 | 760 | 11,700 | 0.217 | 19,300 | 110 | 84.5 |
| 0.0 | 763 | 8800 | 0.143 | 14,600 | 78.5 | 60.2 |
| 3.0 | 763 | 8100 | 0.149 | 13,200 | 65.8 | 50.4 |
| 5.0 | 763 | 7650 | 0.191 | 12,400 | 73.6 | 56.5 |
| 1.0 | 763 | 5650 | 0.107 | 9280 | 54.7 | 42.0 |
| 2.0 | 763 | 5360 | 0.105 | 8820 | 49.7 | 38.1 |
| 1.0 | 763 | 4880 | 0.107 | 8250 | 54.7 | 42.0 |

TABLE III
VAPORIZATION OF SOLID CYCLOHEXANE AT 0°C.

| Temp. | Pressure | Air rate | $N_A \times 10^5$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 0.0 | 751 | 19,900 | 0.280 | 32,300 | 164 | 118 |
| 0.0 | 751 | 19,700 | 0.293 | 32,100 | 171 | 123 |
| 0.0 | 751 | 19,400 | 0.284 | 31,600 | 165 | 118 |
| 1.0 | 751 | 12,100 | 0.179 | 19,500 | 97.5 | 69.9 |
| 1.0 | 751 | 11,700 | 0.192 | 18,800 | 105 | 75.1 |
| 2.0 | 752 | 6730 | 0.143 | 10,900 | 73.7 | 52.9 |
| 2.0 | 752 | 6560 | 0.146 | 10,600 | 75.5 | 54.1 |
| 3.0 | 752 | 6070 | 0.132 | 9760 | 64.3 | 46.1 |

TABLE IV
VAPORIZATION OF SOLID PHENOL AT 25°C.

| Temp. | Pressure | Air rate | $N_A \times 10^8$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 25.0 | 760 | 24,700 | 4.91 | 32,600 | 180 | 134 |
| 25.0 | 760 | 24,500 | 4.74 | 32,000 | 168 | 125 |
| 25.0 | 760 | 15,600 | 3.38 | 20,400 | 120 | 89.1 |
| 25.0 | 760 | 15,400 | 3.67 | 20,000 | 130 | 96.6 |
| 25.0 | 760 | 15,200 | 3.40 | 19,900 | 120 | 89.5 |
| 25.0 | 760 | 15,200 | 3.74 | 19,900 | 133 | 98.8 |
| 25.0 | 760 | 8700 | 2.34 | 11,400 | 82.6 | 61.5 |
| 25.0 | 760 | 8700 | 2.34 | 11,300 | 79.5 | 59.1 |
| 25.0 | 760 | 8100 | 1.63 | 10,600 | 57.7 | 42.9 |
| 25.0 | 760 | 7860 | 2.10 | 10,200 | 74.5 | 55.5 |
| 25.0 | 760 | 7760 | 1.87 | 10,100 | 69.4 | 49.4 |
| 25.0 | 760 | 5320 | 1.31 | 6930 | 46.5 | 34.6 |

TABLE V
VAPORIZATION OF SOLID CAMPHOR AT 25°C.

| Temp. | Pressure | Air rate | $N_A \times 10^6$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 25.0 | 756 | 29,800 | 2.82 | 38,500 | 219 | 140 |
| 25.0 | 756 | 27,000 | 2.60 | 34,900 | 202 | 129 |
| 25.0 | 756 | 17,500 | 1.83 | 32,500 | 142 | 91.0 |
| 25.0 | 756 | 15,300 | 1.98 | 19,800 | 154 | 98.8 |
| 25.0 | 753 | 9550 | 1.27 | 12,300 | 98.2 | 62.9 |
| 25.0 | 753 | 9500 | 1.18 | 12,200 | 91.6 | 58.6 |
| 25.0 | 753 | 6240 | 0.946 | 8040 | 73.2 | 46.9 |
| 25.0 | 753 | 6210 | 0.937 | 8000 | 72.5 | 46.4 |

TABLE VI
VAPORIZATION OF SOLID *p*-DICHLOROBENZENE AT 15°C.

| Temp. | Pressure | Air rate | $N_A \times 10^6$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 15.0 | 749 | 26,500 | 4.86 | 38,800 | 187 | 130 |
| 15.0 | 749 | 26,300 | 5.00 | 38,500 | 193 | 134 |
| 15.0 | 749 | 13,000 | 3.94 | 19,100 | 113 | 78.5 |
| 15.0 | 749 | 13,000 | 3.02 | 19,100 | 116 | 80.6 |
| 15.0 | 747 | 7860 | 2.27 | 11,500 | 87.1 | 60.6 |
| 15.0 | 747 | 7850 | 2.31 | 11,500 | 77.2 | 53.7 |
| 15.0 | 747 | 5330 | 1.58 | 7800 | 60.8 | 42.3 |
| 15.0 | 747 | 5310 | 1.55 | 7790 | 59.4 | 41.3 |
| 15.0 | 748 | 3880 | 1.12 | 5670 | 42.8 | 29.8 |
| 15.0 | 748 | 3460 | 1.13 | 5070 | 43.4 | 30.2 |

TABLE VII
VAPORIZATION OF SOLID *p*-DICHLOROBENZENE AT 25°C.

| Temp. | Pressure | Air rate | $N_A \times 10^6$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 25.0 | 750 | 27,400 | 14.4 | 38,000 | 195 | 136 |
| 25.0 | 750 | 26,800 | 14.3 | 37,400 | 194 | 135 |
| 25.0 | 750 | 15,400 | 10.0 | 21,400 | 136 | 94.5 |
| 25.0 | 750 | 15,100 | 9.41 | 21,000 | 128 | 88.9 |
| 25.0 | 750 | 8990 | 5.92 | 12,500 | 80.3 | 55.8 |
| 25.0 | 750 | 8930 | 6.05 | 12,400 | 82.1 | 57.1 |
| 25.0 | 750 | 6400 | 4.54 | 8930 | 61.6 | 42.8 |
| 25.0 | 750 | 6410 | 4.69 | 8900 | 63.7 | 44.3 |
| 25.0 | 750 | 3700 | 2.88 | 5150 | 39.1 | 27.2 |

Good correlation is shown in Fig. 4 and the data again offer more evidence for the validity of the Sherwood-Gilliland equation. It will be observed that no deviation of the results from the equation occurred at high Reynolds numbers.

This work as well as that of Sherwood and Gilliland, which was done at values of Schmidt numbers from 0.6 to 2.7, shows that the exponent of the

TABLE VIII
VAPORIZATION OF SOLID *p*-DICHLOROBENZENE AT 35°C.

| Temp. | Pressure | Air rate | $N_A \times 10^6$ | Re | d/x | $\frac{d'/x}{Sc^{0.44}}$ |
|-------|----------|----------|-------------------|--------|-------|--------------------------|
| 35.0 | 756 | 26,900 | 25.0 | 35,400 | 188 | 131 |
| 35.0 | 756 | 26,700 | 26.0 | 35,100 | 195 | 136 |
| 35.0 | 756 | 17,100 | 18.8 | 22,500 | 141 | 98.0 |
| 35.0 | 756 | 17,100 | 18.1 | 22,500 | 136 | 94.4 |
| 35.0 | 757 | 11,100 | 11.8 | 14,600 | 88.4 | 61.5 |
| 35.0 | 757 | 11,100 | 11.6 | 14,500 | 87.3 | 60.7 |
| 35.0 | 757 | 7610 | 9.85 | 10,000 | 73.3 | 51.0 |
| 35.0 | 757 | 7610 | 9.37 | 10,000 | 70.5 | 49.0 |
| 35.0 | 757 | 4910 | 6.13 | 6460 | 46.0 | 32.0 |
| 35.0 | 757 | 4850 | 5.77 | 6380 | 43.1 | 30.0 |

Schmidt number is 0.44. Studies made by Linton and Sherwood (7) with liquids indicate that the Chilton and Colburn (1) exponent of 0.33 represents their data quite satisfactorily. More work is needed to establish the value of the Schmidt number exponent.

The similar behavior of the liquid and the solids warranted a close scrutiny of the Whitman two-film theory (15). It will be remembered that he supposed that all of the resistance to mass transfer in gas-liquid systems existed in two thin laminar layers located on opposite sides of the phase interface. He also believed that the liquid established its equilibrium vapor pressure at the interface and that this condition implied no resistance to mass transfer across the boundary or interface itself. If similar reasoning be adopted for gas-solid systems it would be expected that the same phenomena would exist and that the results could be correlated in a similar fashion.

It is important to note that the results offer a quantitative means of studying sublimation processes. Rates of sublimation and condensation are important in the design of industrial equipment and it is indicated that these may be obtained by the application of the Sherwood-Gilliland equation and from a knowledge of the physical properties of the gasified solid.

Acknowledgments

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Notation

| | |
|--------------|--|
| D | diffusion constant, sq. cm./sec. |
| d | equivalent diameter in the Reynolds number, cm. |
| d' | equivalent diameter for diffusion conditions, cm. |
| k | thermal conductivity, cal./sec. (sq. cm.) ($^{\circ}$ C./cm.) |
| μ | absolute fluid viscosity, gm./cm. (sec.) |
| N_A | diffusion rate, gm-mol./sq. cm. (sec.) |
| P | total pressure, mm. Hg. |
| Δp_A | partial pressure difference of the diffusing component across the stagnant film, mm. Hg. |
| p_{BM} | logarithmic mean of the partial pressure of inert component B at the phase interface and in the bulk of the fluid phase, mm. Hg. |
| R | gas constant, (mm. Hg) (cu. cm.)/(gm-mol.) ($^{\circ}$ K.) |
| Re | Reynold's number, $\frac{du\rho}{\mu}$ |
| ρ | density of the fluid, gm./cu. cm. |
| Sc | Schmidt number, $\frac{\mu}{\rho D}$. |
| T | absolute temperature, $^{\circ}$ K. |
| u | average fluid velocity, cm./sec. |
| x | effective film thickness of the fluid film at the interface, cm. |

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THE PRECIPITATION OF WHEY PROTEINS USING WASTE SULPHITE LIQUOR¹

BY JOHN H. HARE² AND BRUCE E. BAKER³

Abstract

Waste sulphite liquor has been used for recovering whey proteins. The protein precipitating action of sodium lignosulphonate has been compared with that of various other sulphonates. Attempts to isolate the whey proteins from the lignosulphonate complex have been unsuccessful. Preliminary rat-feeding tests indicated that the lignin-protein complex could be well tolerated when it supplied 10% of crude protein in the diet.

Introduction

Lignosulphonic acids have been used in the tanning industry because they have the property of forming insoluble compounds with proteins (1, 3). Wallerstein *et al.* (2) applied these properties to the separation of proteins from wheat mashes after fermentation. Their method consisted of acidifying the mash to pH 1.5-2.0 and subsequently adding waste sulphite liquor. The reaction between the protein and the sulphite liquor took place immediately, and the mixture could be readily filtered. These workers found that up to 90% of the protein combined with the lignin and that the final dried product contained approximately 56% protein. The protein-lignin complex was used in feeding trials and was claimed to have the same nutritive value as the original protein.

Whey is a waste product in the dairy industry in many parts of Canada. It was decided to study the possibilities of Wallerstein's process as a convenient method of recovering proteins of whey.

Materials

The whey used throughout this investigation was obtained from a local muriatic casein plant and when received had a pH value between 4.3 and 4.5.

Samples of sulphite waste were obtained in the liquid form (A) from the Howard Smith Paper Company, Cornwall, Ont., and in the solid form (B) from the Marathon Corporation, Rothchild, Wis. The composition of these two materials appears in Table I.

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TABLE I
COMPOSITION OF SULPHITE WASTE

| Sample A | % | Sample B | % |
|-----------------|-------|-------------------------------------|-------|
| Total solids | 13.18 | Lignin | 61.31 |
| Lignin | 6.59 | Nonreducing carbohydrates | 12.38 |
| Protein | 0.08 | Sulphonic SO ₃ | 12.28 |
| Ash | 1.31 | Sulphonic Na | 3.53 |
| Carbohydrates | 3.29 | Nonsulphonic Na | 2.06 |
| Calcium oxide | 0.63 | CaSO ₄ ·H ₂ O | 2.54 |
| Sulphur dioxide | 1.28 | MgSO ₄ ·H ₂ O | 1.59 |
| | | Na ₂ SO ₄ | 2.97 |
| | | Na ₂ SO ₃ | 0.55 |

Experimental

In order to determine optimum conditions for protein precipitation, 100-ml. samples of whey were measured into 200-ml. centrifuge bottles and different amounts of sulphite liquor added. The materials were thoroughly mixed and then allowed to stand for 10 min. The quantity of protein (6.38) precipitated was determined by centrifuging the mixture and carrying out Kjeldahl determinations on the clear supernatant liquid. Values for protein removal were obtained by subtracting the amount of protein in the supernatant from that of the original whey. The results of these experiments are shown in Table II.

TABLE II
COMPARISON OF WASTE SULPHITE LIQUOR AND SODIUM LIGNOSULPHONATE FOR PRECIPITATION OF WHEY PROTEINS

| | Weight of lignin, gm. | Protein per 100 ml. whey, gm. | Protein in supernatant, gm. | Per cent of total protein precipitated |
|-----------------------------|-----------------------|-------------------------------|-----------------------------|--|
| Waste sulphite liquor, gm. | | | | |
| 1 | 0.066 | 0.771 | 0.495 | 35.8 |
| 2 | 0.132 | " | 0.393 | 49.0 |
| 5 | 0.330 | " | 0.209 | 72.9 |
| 10 | 0.659 | " | 0.204 | 73.5 |
| 15 | 0.989 | " | 0.223 | 71.1 |
| Sodium lignosulphonate, gm. | | | | |
| 0.10 | 0.061 | 0.813 | 0.559 | 31.2 |
| 0.25 | 0.153 | " | 0.358 | 55.9 |
| 0.50 | 0.305 | " | 0.181 | 77.7 |
| 1.25 | 0.763 | " | 0.147 | 81.9 |
| 2.50 | 1.525 | " | 0.208 | 74.4 |

Effect of pH

A series of experiments were carried out to study the effect of pH on the precipitation of whey proteins. One-hundred ml. samples of whey were adjusted at various pH values (1.8-5.1) and then 1.2 gm. of sodium lignosul-

phonate (Sample B) was added. The same procedure was followed for determining the amount of protein precipitated as outlined in the previous experiment. The results are shown in Fig. 1.

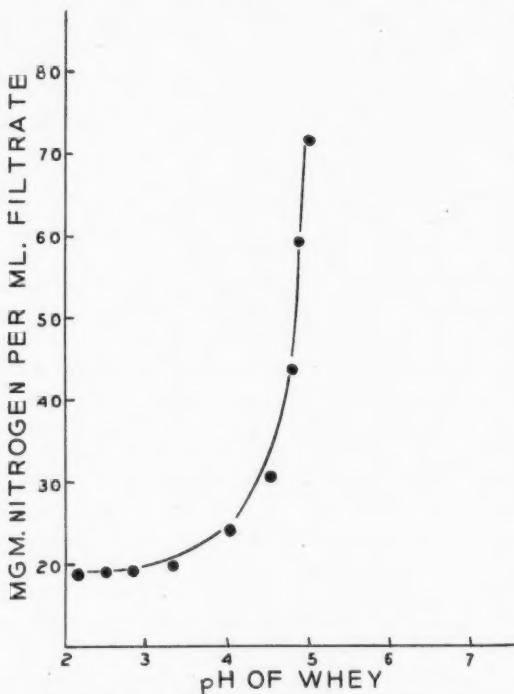


FIG. 1. Effect of pH on the precipitation of whey proteins. The pH values of the whey were measured before the addition of sulphite waste (1.2 gm. per 100 ml. whey).

Comparison with Other Precipitants

The protein precipitating action of the solid lignosulphonate was compared with that of several other sulphonates. Equivalent weights of sodium benzene sulphonate (180 mgm.), sodium-1, 2-naphthoquinone-4-sulphonate (260 mgm.), sodium anthraquinone- β -sulphonate (310 mgm.), and sodium lignosulphonate (1200 mgm.) were added to 100-ml. samples of whey. The amount of protein precipitated was determined as before. It will be noted in Table III that on an equivalent basis sodium lignosulphonate is considerably more effective than the other sulphonates.

Studies on the Lignosulphonate Protein Complex

The lignosulphonate-protein complex obtained from the treatment of whey with sulphite liquor was washed and freeze-dried. This product was a light brown powder containing about 60% protein ($N \times 6.38$). It had a fairly pleasant odor and taste. There was no indication that the complex was soluble

TABLE III
PROTEIN PRECIPITATING ACTION OF VARIOUS SULPHONATES

| Precipitant | Per cent of total protein precipitated |
|---|--|
| Sodium lignosulphonate | 71.2 |
| Sodium benzene sulphonate | 14.1 |
| Sodium-1, 2-naphthoquinone-4-sulphonate | 51.7 |
| Sodium anthraquinone- β -sulphonate | 46.6 |

in any of the common solvents, but when added to dilute alkali it readily went into solution.

A preliminary attempt to separate the lignin from the protein was carried out by adding known protein and/or lignin precipitants to a slightly alkaline solution of the precipitated protein. In most cases a precipitate was formed, but on analysis the precipitate proved to be similar to the original material in protein content. This suggested that the protein was not bound to the lignosulphonate by a simple salt linkage, but was firmly attached even in alkaline solution. The protein content of the complex was not appreciably affected by repeated re-solution and precipitation. Such changes as were observed indicated a slight decrease in protein content.

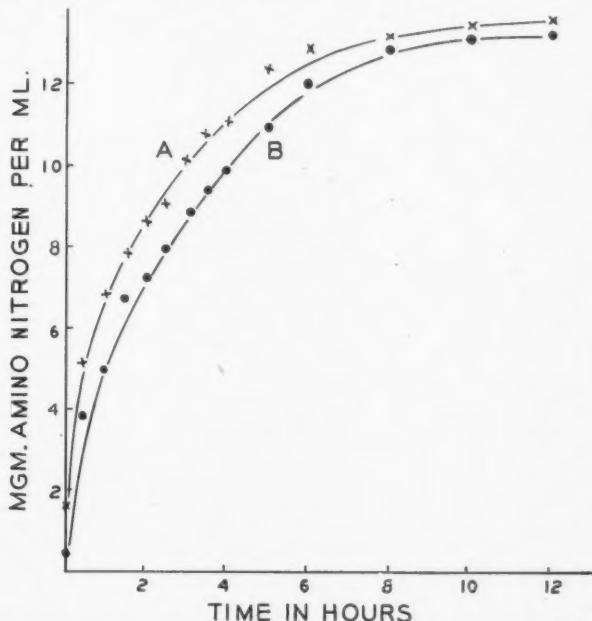


FIG. 2. Comparison of the hydrolysis of commercial lactalbumin and the lignosulphonate-protein complex. Curve A—lactalbumin; Curve B—lignosulphonate-protein complex. The amino nitrogen values indicate the number of milligrams of amino nitrogen per ml. of hydrolyzing mixture.

Acid hydrolysis of the material proceeded at a rate similar to that of crude lactalbumin. It was noted that the ratio of amino nitrogen (Van Slyke nitrous acid method) to total nitrogen at the beginning of the hydrolysis was lower with the complex than with crude lactalbumin. This would indicate that the lignosulphonate was attached to free amino groups of the whey protein. Fig. 2 shows a typical acid hydrolysis curve for the lignin-protein material as compared with that of commercial lactalbumin containing the same amount of protein.

Preliminary rat-feeding tests were based on the use of a control diet containing starch 75%, casein 20%, minerals 4%, fish oil 1%. In the test groups the casein was either completely replaced by 40% lignin-protein complex, partially replaced by 20% lignin-protein complex or 10% lignin-protein complex. (The lignin-protein complex contained 50% crude protein.) The rats ate all the diets readily, but the group receiving 40% of the lignin-protein complex developed severe diarrhoea and the diet was clearly deleterious. The group receiving 20% had slight diarrhoea, but otherwise remained in good condition. The rats receiving 10% remained normal. From these preliminary tests it was concluded that, although high levels of the lignin-protein complex are likely to be deleterious, lower levels designed to supply up to about 10% of crude protein in the diet may be well tolerated. These experiments were not sufficiently extensive to provide information as to the nutritive value of the lignin-protein material.

Discussion

It has been shown that waste sulphite liquor may be used as a precipitant for whey proteins. The whey does not have to be heated nor the pH of the whey adjusted when it is a by-product in the manufacture of acid coagulated casein. The lignin-protein complex can be separated easily from solution and readily dried. The method seems to be a more convenient means of recovering whey proteins than the heat coagulation method when it is to be used as a protein supplement in animal feeding.

The fact that the percentage removal of protein ($N \times 6.38$) from the whey increased with increasing quantity of protein present indicates that there was a small amount of nitrogenous material in the whey which remained fairly constant and was not precipitated by the lignosulphonate.

Acknowledgments

The authors wish to express their thanks to Dr. W. D. McFarlane for his continued interest in this work and for many helpful suggestions. The authors are also indebted to the Champlain Milk Company for a Research Grant.

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AN X-RAY DIFFRACTION LAUE MICROCAMERA¹

BY WILLIAM H. BARNES AND SYDNEY WAGNER²

Abstract

A microcamera for obtaining symmetrical transmission and back reflection Laue photographs of single crystals of microdimensions is described. The camera design is similar to that of the Chesley-Philips microcamera with the important additions of a back reflection film holder and a goniometer assembly and improved transverse controls for the specimen.

Introduction

The instrument described in this paper was designed to obtain symmetrical back reflection and transmission X-ray diffraction Laue photographs for the identification of unknown single microcrystals. Since the crystals frequently do not have well developed faces it usually is impossible to orientate them by optical methods. Thus, when the crystals are first mounted in the camera, important crystallographic directions generally have random orientations with respect to the X-ray beam. In the new camera provision is made for setting the specimen by means of two angular controls at right angles to each other. The angular adjustment of the crystal is effected by means of back reflection photographs, which are more useful than transmission ones because the pattern on the back reflection film is less sensitive to an angular change of the specimen than is the transmission pattern. The general design of the camera is similar to that of the Chesley-Philips microcamera (1) with the important exception that it incorporates a back reflection film holder, a simple goniometer assembly and improved transverse motions of the specimen. It is slightly larger in overall dimensions but since Dural has been used whenever possible it is somewhat lighter than the Chesley-Philips model.

Description of Camera

A cutaway drawing of the camera is shown in Fig. 1.

The microcrystal is cemented with Household Cement to the end of a Pyrex glass fiber about one inch in length and 0.5 mm. to 0.2 mm. in diameter. The other end of the fiber is inserted into its holder (1, Fig. 1) and is held firmly in place with plasticine. This places the specimen about 2 mm. from the end of the glass collimator shown at 2, Fig. 1. The collimator consists of a piece of barometer tubing, about 8 mm. long and 50 μ bore, one end of which is tapered to assist in loading the back reflection film and the other fits into a brass holder. The end towards the X-ray tube is covered, except for the bore opening, with

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lead foil; the other end is similarly covered except for a hole to allow passage of the tapered tip. Two mutually perpendicular translation controls (3 and 4, Fig. 1) enable the crystal to be brought into the center of the X-ray beam. Angular orientation of the specimen about two axes at right angles is effected

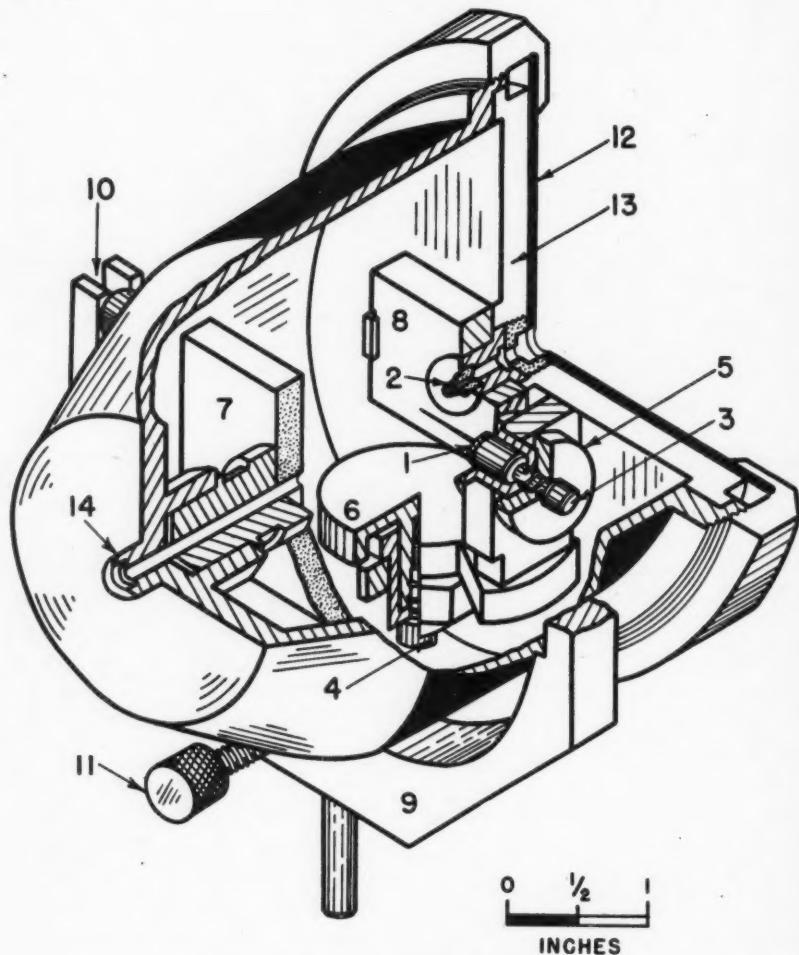


FIG. 1. Cutaway drawing of microcamera.

by the rotation controls 5 and 6, Fig. 1. The transmission film holder (7, Fig. 1) in the original camera could be located to give an effective crystal-to-film distance of either 24.4 mm. or 28.6 mm. Recently it has been altered to slide on a tube and, by means of a setscrew, the crystal-to-film distance can be fixed anywhere between 18.3 mm. and 25.5 mm. The photographic film is held in

place on the flat face of the transmission holder by means of two small pieces of scotch tape. The back reflection film holder (8, Fig. 1) is 5.8 mm. from the specimen. Holes for passage of the undiffracted beam through the transmission film and of the collimator through the back reflection film are made with a ticket punch. After pushing the back reflection film into place over the collimator the side edges are slipped under narrow strips to hold the film against the face of the cassette. The assembled camera is light-tight and is loaded in the dark room so that the films need no black paper protection.

As in the Chesley-Philips microcamera, the fork (9, Fig. 1) on which the camera is held by two swivel pins (10, Fig. 1, one only indicated) can be rotated in its stand (see Fig. 3), while a screw (11, Fig. 1) provides a tilt control. These two motions enable the camera to be adjusted so that the most intense portion of the incident X-ray beam passes through the bore in the glass collimator. The remainder of the beam is absorbed by the brass collimator holder and a lead protecting screen (12, Fig. 1) which covers the face of the camera (13, Fig. 1). To aid in adjusting the camera in the beam, an exit tube (14, Fig. 1) fitted with a fluorescent screen and a protecting disc of lead glass is provided.

The face of the camera (13, Fig. 1), carrying the collimator and the specimen holder with its controls, may be placed on the stage of an optical microscope, as illustrated in Fig. 2, for alignment of the specimen over the center of the collimator.

The camera is shown in operating position on a Philips diffraction unit in Fig. 3.

Procedure and Typical Results

The diffraction spots arising from one zone in a crystal lie along a hyperbola on the back reflection film (2) and this hyperbola degenerates into a straight line when it passes through the center of the film. For any random orientation of the specimen with respect to the X-ray beam the pattern of spots on the back reflection film shows no symmetry. It is generally possible, however, to locate at least one point on the photograph lying at the intersection of three or more hyperbolae. Such a point is marked by a diffraction spot usually of greater intensity and more remote from its neighbors than the other spots on the film. It represents an important crystallographic direction in the crystal and the general procedure is to change the orientation of the crystal by means of the angular controls so as to move this spot to the center of the film. The pattern on the resulting back reflection photograph usually is no longer completely random and frequently shows at least one symmetry line passing through the center of the film. Prominent (*i.e.*, more intense) spots along this line are moved successively to the center of the film by controlled orientation of the crystal until maximum symmetry of the complete back reflection pattern is obtained. A transmission Laue photograph is then taken and the negative is enlarged to an effective crystal-to-film distance of 5 cm. (for example, see Fig. 4C). From a gnomonic projection (3) the axial ratio of the crystal is deter-

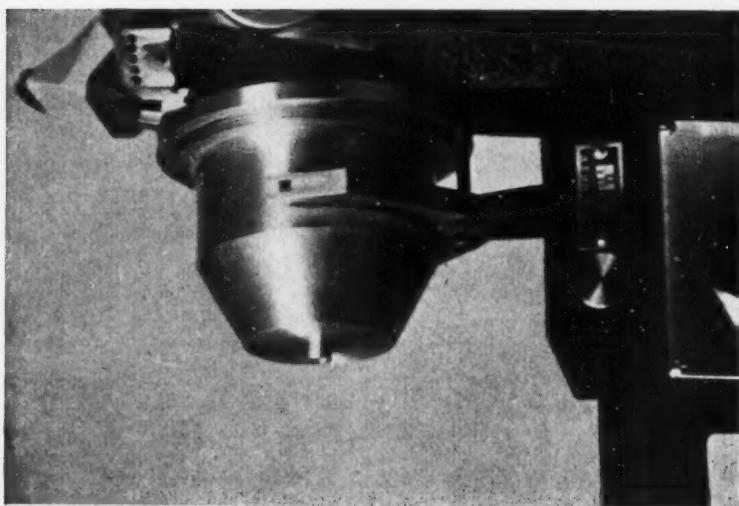


FIG. 3. Microcamera on diffraction unit.

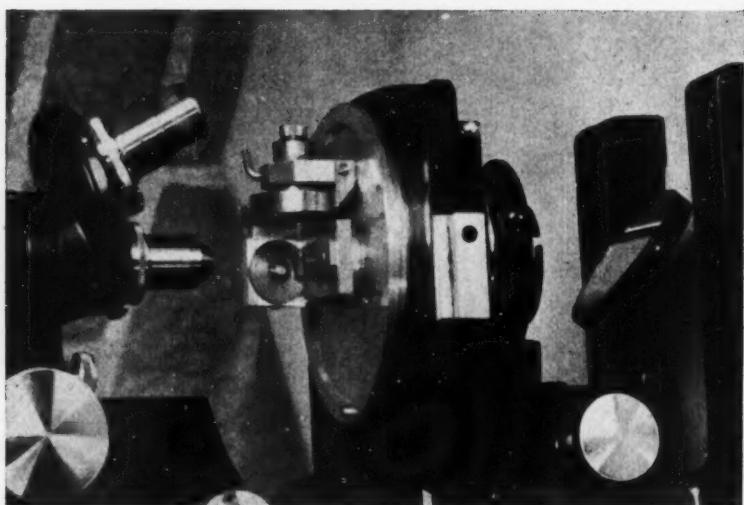


FIG. 2. Microcamera face on microscope.

PLATE I

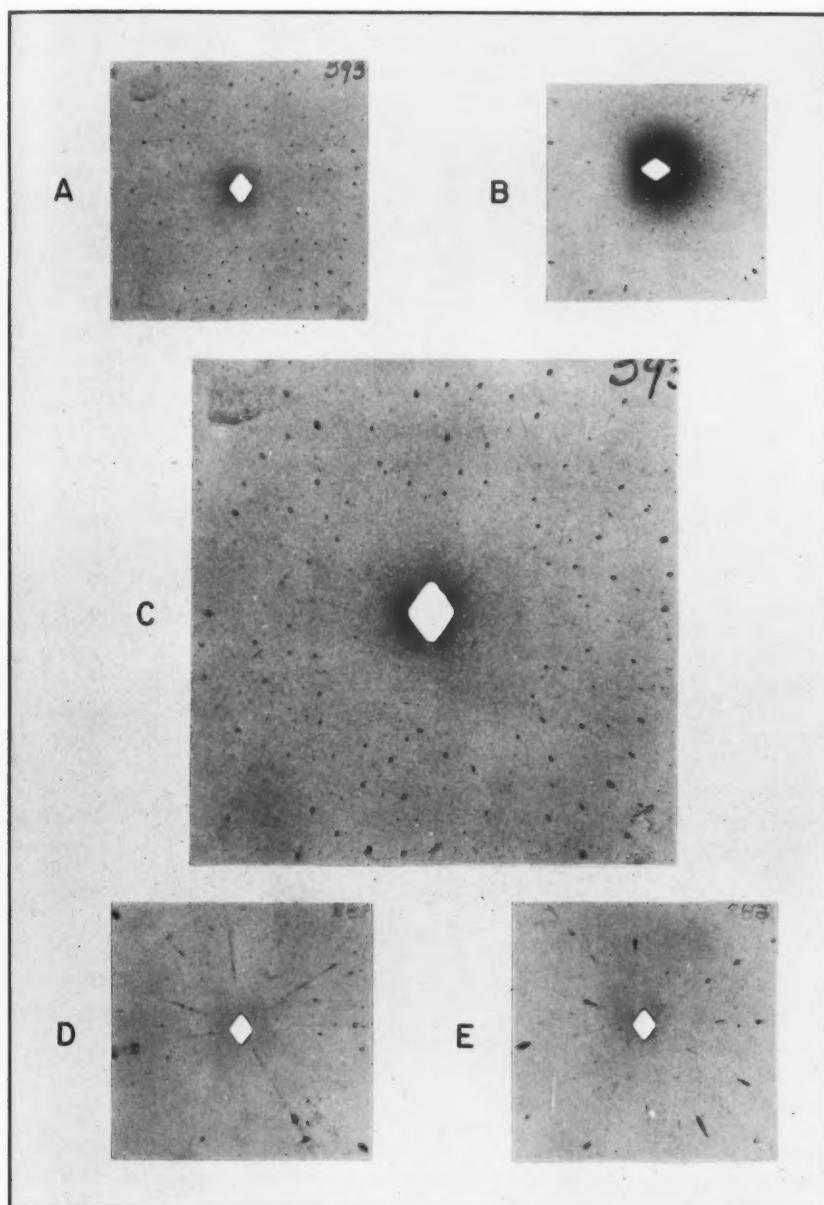
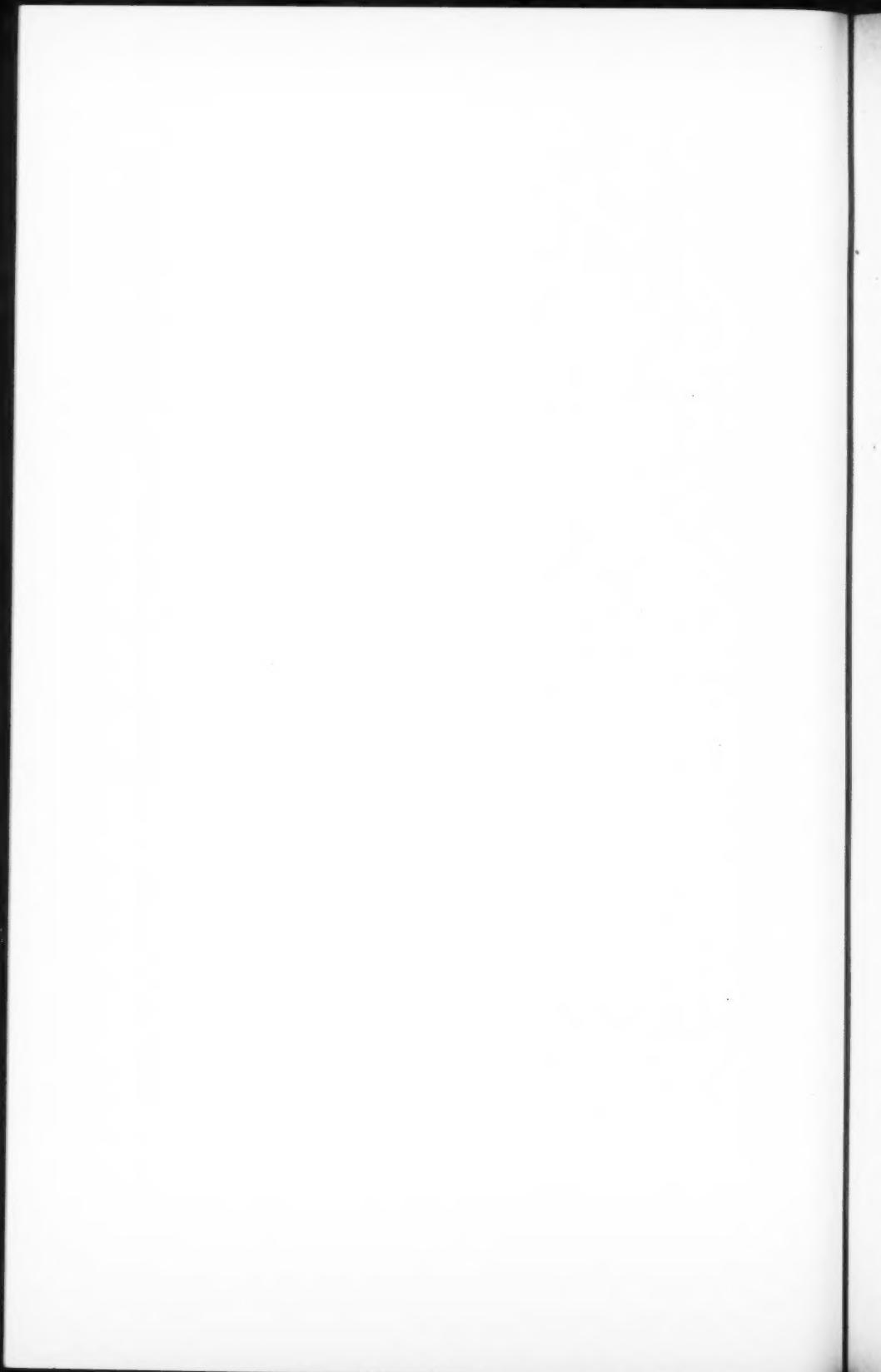


FIG. 4. *A, B, D, E—Laue microphotographs; C—enlargement of A.*



mined. The symmetry of the Laue pattern and the axial ratio are used to eliminate all but a relatively few crystals from further consideration. Final identification of the unknown microcrystal is effected by direct comparison of its transmission Laue pattern with those of known macrocrystals.

The use of Greninger charts (2) as an aid during the orientation of the particular crystals for which the camera primarily was built is excluded by the fact that their identities, and hence their crystal systems and axial ratios, are unknown at the stage when such charts would be useful.

The camera is being employed successfully in a study of the crystal nuclei of pleochroic haloes and other inclusions in mica. For example, the transmission and back reflection Laue photographs of a crystal with approximate dimensions $80 \times 60 \times 50\mu$ are shown in Fig. 4A and in Fig. 4B, respectively. This crystal had been removed from the mica before it was mounted in the camera.

The transmission pattern obtained from a halo nucleus crystal (approximately, $40 \times 20 \times 20\mu$) which was examined while still embedded in the mica is reproduced in Fig. 4D. In this case the fragment of mica containing the crystal was placed in the camera. By means of the translation controls Laue photographs of areas of the mica adjacent to the pleochroic halo with its nucleus, and free from other inclusions, could be obtained at all stages during the orientation of the crystal nucleus. The final transmission photographs are shown in Fig. 4; one with the X-ray beam passing over the orientated crystal and through the mica (Fig. 4D), the other with the beam passing through the mica alone (Fig. 4E). There is no difficulty, particularly on the original negative, in distinguishing between the spots due to the crystal nucleus and those due to the mica.

Exposure times with tungsten radiation at about 50 kv. and 14 ma. vary from four or five hours for larger crystals, such as the ones employed for Fig. 4, to 20 hr. or more for smaller ones of the order of 15μ in longest dimension, the smallest so far handled.

Discussion

One of the features of the camera is the simplicity of the angular controls for orientation of the crystal. One (6, Fig. 1) corresponds to the rotation axis of standard single crystal equipment although it covers an angle of only 190° of which the center 60° cannot be used because it is occupied by the objective lens of the microscope during alignment of the specimen over the collimator. The other (5, Fig. 1), corresponding to one arc of a conventional goniometer head, however, has a full range of 360° which is very much greater than that commonly provided. A standard goniometer head, of course, has the advantage of a second arc, the axis of which is at right angles to that of the other arc and to the rotation axis. This convenience, however, is largely outweighed by the difficulty, and expense, of making such a head on a microscale.

The camera has been very useful in the identification of those microcrystals to which it has been applied. So far only specimens belonging to the tetragonal and hexagonal systems have been encountered, but there should be no difficulty with cubic, orthorhombic, or monoclinic specimens. The orientation and subsequent identification of triclinic crystals would, as usual, be more troublesome.

Acknowledgments

The camera was made in the Physics Division Workshops under the supervision of Mr. W. J. MacKay. Mr. H. N. Lachance of the Central Draughting Office did the excellent cutaway drawing reproduced in Fig. 1, and Mr. A. W. Hanson took the photographs shown in Figs. 2 and 3. Mr. J. W. Forsyth and Mrs. H. M. Sheppard assisted in the preparation of prints and enlargements.

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THE EMULSION POLYMERIZATION OF ISOPRENE. II¹

BY WARREN L. REYNOLDS,² ARTHUR L. JOHNSON, AND R. H. CLARK

Abstract

The effect of cumene hydroperoxide, various mercaptans, disulphides, and diazothioethers upon the polymerization of isoprene has been investigated. The half decomposition period of certain of the ethers was measured.

Introduction

This study of the emulsion polymerization of isoprene was conducted with two purposes in view. The first was to increase the molecular weight of the polyisoprene resulting from cumene hydroperoxide initiation while at the same time keeping the gel content low.

The possibilities for obtaining this objective were thought to be three. The first was decreasing the modifier content.

The second was decreasing the amount of initiating reagent present and thereby decreasing the rate of the initiation reaction (6). However, a decrease in the initiation rate must be simultaneously accompanied by a decrease in the termination rate, i.e., a decrease in the amount of initiation reagent must be accompanied by a decrease of modifier content, or a decrease in the molecular weight would result because of the relatively high rate of termination.

The third possibility was decreasing the amount of soap. A decrease in the soap content decreases the number of reaction loci (5) and should, therefore, decrease the initiation rate since, according to the theory of Wall and Swoboda (9), an initiating free radical is produced only when ferrous iron enters a locus and reacts with the organic peroxide. As stated above, a decrease of the initiation rate must be simultaneously accompanied by a decrease of the termination rate, i.e., a decrease of soap content must be accompanied by a decrease of modifier content, or a decrease of the molecular weight would result.

The second purpose of the investigation was to test various mercaptans, disulphides, and diazothioethers as initiating agents. The yields obtained with these reagents were compared with their rates of thermal decomposition in a few cases where this was possible.

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² Holder of a National Research Council Bursary.

Experimental Procedures

The cumene hydroperoxide (CHP) formula used was:

| | | |
|---|----------|-----------------|
| Water | 195 | parts by weight |
| Isoprene | 100 | " " |
| Glucose | 1.0 | " " |
| FeSO ₄ .7H ₂ O | 0.1 | " " |
| Na ₄ P ₂ O ₇ .10H ₂ O | 1.0 | " " |
| CHP | variable | |
| Mix tertiary mercaptan | (M.T.M.) | |
| R.R.C. soap | variable | |
| (Rubber Reserve Corporation) | | |
| Polymerization temperature | 45°C. | |

The order of addition was: soap solution, glucose solution, ferrous sulphate, and sodium pyrophosphate together in solution, CHP, MTM, and then isoprene. Air was excluded by boiling all water immediately prior to use and by flushing the bottles with isoprene vapor. Bottles (16 oz.) provided with composition, cork-lined, screw caps were used. Agitation was provided by end over end motion of the bottles, 18 times per minute, in a thermostat. The yields were measured by determining the total solids with an allowance being made for the other solids present. Coagulation was effected with a brine-acid solution of previously reported composition (1). The crumb was washed with hot water and dried in a vacuum at 35°C. for 48 hr. The intrinsic flow time was measured by the conventional method (2). The gel content was measured by the method of Medalia and Kolthoff (8) except that the above noted drying temperature and period were used in place of those recommended by them. The reason for this was that heat breakdown of the polymer occurred above 45°C.

The formula and procedure used for polymerizations with the mercaptans and disulphides was that reported for dodecylmercaptan (1) with the mercaptans and disulphides substituted for the latter.

Didodecyldisulphide was prepared by the method of Fore and Bost (4). Phenylmercaptan was prepared by reducing benzene sulphonylchloride with tin and hydrochloric acid. The mercaptan was steam distilled, extracted with ether, and redistilled at 166°–170°C. Diphenyldisulphide was prepared by the oxidation of phenylmercaptan and, after recrystallization, had a.m.p. of 61±1°C.

The procedure used in employing the diazothioethers as initiating reagents consisted of dissolving 4.5 gm. of R.R.C. soap in 200 ml. of water by heating, cooling the soap solution to 25°C., and adding 100 gm. of isoprene containing the dissolved diazothioether. The polymerizations were made at 45°C. The amount of the particular diazothioether used in the formula was based on a weight equivalent of one gm. of *p*-methyl benzene diazothio- β -naphthol.

The β -thionaphthol required in the synthesis of some of the diazothioethers was made from sodium β -naphthalene sulphonate by converting the sodium salt to the corresponding chloride with PCl_5 at 150°C ., recrystallization of the chloride from chloroform, and reduction of the chloride with tin and hydrochloric acid. The sodium β -naphthalene sulphonate was prepared by the method of Witt (10). The β -thionaphthol was steam distilled and recrystallized from alcohol; m.p. $82 \pm 1^\circ\text{C}$. The thio- p -cresol was prepared from sodium p -toluene sulphonate, which was converted to the corresponding acid chloride, and then reduced to the mercaptan as above. The sodium p -toluene sulphonate was prepared by the method given by Fieser (3). The mercaptan was recrystallized from alcohol m.p. $42^\circ \pm 1^\circ\text{C}$. The diazothioethers were prepared using the standard methods of diazotization and coupling.

Results and Discussion

The results of the three possible methods for increasing the molecular weight given in the introduction are listed in the tables: I, II, and III.

A decrease of soap content from 4.2 parts to 3.0 parts affected an increase in the intrinsic flow time. A decrease in the CHP content caused little change

TABLE I
VARIATION OF M.T.M. AND POLYMERIZATION TIME
WITH 0.17 PART CHP AND 4.2 PARTS R.R.C. SOAP

| Sample | P'z'n time, hr. | % Yield | % Gel | Intrinsic viscosity | M.T.M., gm. |
|--------|-----------------|---------|-------|---------------------|-------------|
| 1 | 5.0 | 81 | 77 | 1.18 | 0.45 |
| 2 | 5.0 | 82 | 1 | 1.48 | 0.56 |
| 3 | 5.0 | 82 | 1 | 1.19 | 0.68 |
| 4 | 5.5 | 84 | 80 | 1.21 | 0.45 |
| 5 | 5.5 | 86 | 1 | 1.65 | 0.56 |
| 6 | 5.5 | 85 | 1 | 1.35 | 0.68 |
| 7 | 6.0 | 93 | 77 | 1.12 | 0.45 |
| 8 | 6.0 | 93 | 1 | 2.29 | 0.56 |
| 9 | 6.0 | 91 | 1 | 1.82 | 0.68 |
| 10 | 6.5 | 96 | 85 | 1.17 | 0.45 |
| 11 | 6.5 | 90 | 1 | 2.12 | 0.56 |
| 12 | 6.5 | 93 | 1 | 1.76 | 0.68 |

in the intrinsic flow time. This latter result would seem to indicate that the initiation rate was not appreciably affected by the decrease and is in accordance with the observation of Kolthoff and Medalia (7) who found that decreasing the CHP content of a butadiene-styrene formula did not change the initiation rate but only the yield obtainable if the CHP content was below the minimum amount required for a high yield.

When sufficient modifier is present to prevent the formation of gel, the maximum intrinsic flow time values obtained in the hydrogen peroxide, anodic

TABLE II
VARIATION OF M.T.M. AND POLYMERIZATION TIME
WITH 0.1 PART CHP AND 4.2 PARTS R.R.C. SOAP

| Sample | P'z'n time, hr. | % Yield | % Gel | Intrinsic viscosity | M.T.M., gm. |
|--------|-----------------|---------|-------|---------------------|-------------|
| 13 | 6.0 | 72 | 72 | 1.12 | 0.23 |
| 14 | 7.0 | 76 | 75 | 1.19 | 0.23 |
| 15 | 8.0 | 74 | 72 | 1.06 | 0.23 |
| 16 | 5.0 | 69 | 52 | 1.19 | 0.28 |
| 17 | 6.0 | 72 | 55 | 1.12 | 0.28 |
| 18 | 5.0 | 68 | 39 | 2.35 | 0.34 |
| 19 | 5.5 | 70 | 71 | 1.20 | 0.34 |
| 20 | 6.0 | 71 | 54 | 2.04 | 0.34 |
| 21 | 5.0 | 79 | 40 | 1.09 | 0.39 |
| 22 | 6.0 | 80 | 69 | 0.87 | 0.39 |
| 23 | 7.0 | 82 | 72 | 1.07 | 0.39 |
| 24 | 5.0 | 81 | 35 | 2.28 | 0.45 |
| 25 | 6.0 | 82 | 2 | 2.33 | 0.45 |
| 26 | 7.0 | 79 | 3 | 2.22 | 0.45 |

TABLE III
VARIATION OF M.T.M. AND POLYMERIZATION TIME
WITH 0.17 PART CHP AND 3.0 PARTS R.R.C. SOAP

| Sample | P'z'n time, hr. | % Yield | % Gel | Intrinsic viscosity | M.T.M., gm. |
|--------|-----------------|---------|-------|---------------------|-------------|
| 27 | 5.0 | 82 | 74 | 1.48 | 0.30 |
| 28 | 6.0 | 90 | 73 | 1.40 | 0.30 |
| 29 | 5.5 | 86 | 74 | 1.12 | 0.34 |
| 30 | 6.0 | 90 | 72 | 1.03 | 0.34 |
| 31 | 6.5 | 92 | 73 | 0.90 | 0.34 |
| 32 | 5.0 | 82 | 63 | 0.87 | 0.38 |
| 33 | 6.0 | 89 | 63 | 0.94 | 0.38 |
| 34 | 5.5 | 86 | 2 | 2.51 | 0.45 |
| 35 | 6.0 | 90 | 4 | 2.63 | 0.45 |
| 36 | 6.5 | 92 | 5 | 2.60 | 0.45 |

oxidation (1), and CHP formulae are approximately 2.8, 2.9, and 2.6, respectively, and are not widely different. In the air oxidation formula (1) a range of intrinsic flow time values up to 4.3 was obtained.

The results of employing mercaptans and disulphides as initiating reagents are given in Table IV. The results are for 24 hr. of polymerization at 45°C.

The ineffectiveness of the aromatic mercaptans as initiators is probably due to the ease with which they are oxidized to the disulphide and it is seen that the disulphides, at best, have but poor initiating ability.

The results of employing diazothioethers are given in Table V.

TABLE IV
USE OF VARIOUS MERCAPTANS AND
DISULPHIDES AS INITIATORS

| Sample | Modifier | % Yield |
|--------|---|------------|
| 1 | 0.2 gm. C ₁₂ H ₂₅ SH | 70 |
| 2 | " " | 72 |
| 3 | " " | 73 |
| 4 | 0.2 gm. C ₁₂ H ₂₅ S-S-C ₁₂ H ₂₅ | 10 |
| 5 | " " | 10 |
| 6 | " " | 9 |
| 7 | 0.2 gm. C ₆ H ₅ SH | Negligible |
| 8 | " " | " |
| 9 | 0.2 gm. C ₆ H ₅ S-S-C ₆ H ₅ | 0 |
| 10 | " " | 0 |
| 11 | 0.2 gm. CH ₃ C ₆ H ₅ SH | 0 |
| 12 | 0.2 gm. C ₁₀ H ₇ SH | 0 |

TABLE V
USE OF DIAZOTHIOETHERS AS INITIATING AGENTS

| Initiating reagent | P'z'n time, hr. | % Yield | % Gel |
|---|-----------------|------------------|-------------|
| 0.87 gm. <i>p</i> -CH ₃ -C ₆ H ₄ -N = N-S-C ₆ H ₄ -CH ₃ | 9 | { 88 91 90 | 0 0 0 |
| 1.00 gm. <i>p</i> -CH ₃ -C ₆ H ₄ -N = N-S-C ₁₀ H ₇ | 9 | { 70 68 68 | 0 |
| 1.08 gm. <i>p</i> -Br-C ₆ H ₄ -N = N-S-C ₆ H ₄ -CH ₃ | 24 | { 36 36 38 | 0 0 0 |
| 1.23 gm. <i>p</i> -Br-C ₆ H ₄ -N = N-S-C ₁₀ H ₇ | 24 | { 27 27 18 | 0 0 0 |
| 1.08 gm. <i>p</i> -NO ₂ -C ₆ H ₄ -N = N-S-C ₁₀ H ₇ | 24 | { 5 5 5 | 0 0 0 |
| 1.08 gm. <i>o</i> -NO ₂ -C ₆ H ₄ -N = N-S-C ₁₀ H ₇ | 24 | { 5 5 5 | 0 0 0 |

The rate of thermal decomposition of some of the diazothioethers was measured by observing the rate of evolution of nitrogen from a solution of the ether in 100 ml. of butyl phthalate. The three diazothioethers tested did not decompose appreciably at 45°C. A temperature of 65°C. was chosen, since it provided a convenient rate of decomposition for the ethers measured.

The thermal decomposition of *p*-methyl benzene diazothio-*p*-cresol, *p*-methyl benzene diazothio- β -naphthol, and *p*-bromobenzene diazothio-*p*-cresol were measured. There was a notable induction period during which no nitrogen was evolved for each of the above compounds. This period was 970, 1560, and 4590 seconds respectively. The half decomposition period for each compound was 42 ± 1 , 82 ± 1 , and 212 ± 3 min. respectively.

The length of the observed induction period and the time required for half decomposition parallel approximately the ability of the diazothioethers to initiate polymerization of isoprene for the ethers investigated. The order of activity as shown in Table V conforms with the resonance theory. The ethers formed by coupling with thio- β -naphthol are more stable than those formed by coupling with thio-*p*-cresol. The presence of *p*-Br and *o*- and *p*-nitro groups in the amine part of the molecule greatly reduces the effectiveness of the ether by increasing the resonance energy.

Measurements on the rates of decomposition of the diazothioethers were discontinued, since the rates of decomposition were found to be influenced by surface area. However, since the rates of decomposition were measured under similar conditions they do afford a relative comparison of the stabilities of the ethers.

Acknowledgment

The authors are very grateful to the National Research Council of Canada for the financial assistance that has made this investigation possible. They also wish to thank the Research and Development Division of Polymer Corporation, Sarnia, for its valuable assistance.

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THE EMULSION POLMERIZATION OF ISOPRENE

III. THE MEASUREMENT OF THE AMOUNT OF VINYL GROUPS¹

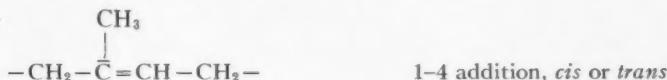
BY NORMAN E. PHILLIPS² AND R. H. CLARK

Abstract

An improved method of calculating the amount of vinyl groups in a polymer from its rate of reaction with perbenzoic acid is presented and used to compare three types of emulsion polyisoprene with natural rubber.

The physical properties of various polymers are intimately associated with their structures. The work described in this paper is a comparison of the structure of polyisoprenes prepared in these laboratories by various catalyst systems (2, 12).

When isoprene polymerizes each monomer molecule can enter the polymer molecule in any of the following four ways:



Both 1-2 and 3-4 addition result in the formation of vinyl side groups. Natural rubber has been shown to be almost entirely *cis*, 1-4 polyisoprene. In comparing synthetic polymers, it is important to have an accurate method for the determination of 1-4 addition. Several methods that have been suggested and used for this determination are,

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- (a) Polymerization of equimolecular quantities of monomer and modifier (9),
- (b) Ozone degradation (5, 10, 11),
- (c) Infrared absorption spectra (3, 4),
- (d) Perbenzoic acid titration (7, 13, 14).

The perbenzoic acid method was selected for use in these experiments.

The reaction of perbenzoic acid with an ethylene is of the second order, and the rate depends markedly on the groups attached to the carbon atoms of the double bond. Ethylenes that have positive groups, such as alkyl groups, attached to the carbon atoms of the double bond, react more rapidly. For this reason the double bonds in a polymer formed by 1-4 addition react more rapidly than the vinyl groups.

Kolthoff and Lee (7), and later Saffer and Johnson (13), have used this difference in the rates of reaction to measure the percentage of vinyl groups in polymers.

The methods of calculating the percentage of vinyl groups, used by Kolthoff and Lee, depend on an extrapolation of the graph of double bonds oxidized versus time. For a mixture of vinyl groups and internal double bonds this graph should rise rapidly until all the internal double bonds have reacted, and then more slowly while the vinyl groups react. A tangent to the flat, slowly increasing part of the curve, should cut the axis, time = 0, at close to the initial concentration of internal double bonds. Kolthoff and Lee allowed a mixture that was 0.02 M in double bonds and 0.03 M in perbenzoic acid to react at 0°C. They made the approximation that the rate of reaction of the external double bonds could be expressed by the second order rate equation with $(P-I)$ substituted for P for the initial concentration of perbenzoic acid.

P = initial concentration of perbenzoic acid,

I = initial concentration of internal double bonds,

E = initial concentration of vinyl groups,

A = total initial concentration of double bonds, $= I + E$.

X = concentration of external double bonds oxidized at time t .

$$kt = \frac{1}{(P-I)-E} \quad 2.303 \log \frac{E(P-I-X)}{(P-I)(E-X)} \quad (1)$$

This equation would be correct if the internal double bonds reacted instantly but actually the concentration of perbenzoic acid would be reduced to $(P-I)$ only after several hours.

Using Equation (1) together with the approximate values of I and E obtained from the extrapolation of the rate curve, Kolthoff and Lee calculated the value of the rate constant k for various values of t . They then used the average of the calculated values of k to construct a calibration curve that gave the percentage of vinyl groups in a polymer from the fraction of the total concentration of double bonds oxidized in a certain time.

The rate curve is, of course, not a straight line, and the value of I obtained by the extrapolation depends on the time at which the tangent is drawn. The error in the approximate value of I obtained from the extrapolation may produce only a small error in the calculated value of k , but this error in k will produce an error in the results calculated from the calibration curve of the same size as that in the extrapolation. Furthermore, taking the average of a number of calculated values of k does not decrease the error if all the values of k are based on the same value of I .

It was felt that there should be a more accurate method for calculating the amount of vinyl groups present that did not depend on an extrapolation of the rate curve. The method to be described below has been used to compare the amounts of vinyl groups in several samples of polyisoprene prepared in these laboratories, and it appears to offer some advantages.

The exact rate equation for the reaction of a polymer sample containing two kinds of double bonds with perbenzoic acid would be that for a mixture of two reactants in competing reactions for a third reactant. This equation would be too complicated to be useful and therefore an approximate treatment is necessary. The same assumptions that Kolthoff and Lee made in using the second order rate equation can be shown to be justified. In a solution that is 0.03 M in perbenzoic acid and 0.02 M in double bonds that react with a rate constant of 100 liter m.⁻¹ hr.⁻¹, the double bonds would be 99% oxidized in 3.52 hr.; but if the rate constant was 0.5, only 5.1% would be oxidized in the same time. If the solution had been 0.02 M in a mixture of about 80% internal and 20% external double bonds, the internal double bonds would be oxidized in roughly the same time. The external double bonds would react more slowly, both because of their lower concentration and because the concentration of perbenzoic acid would decrease rapidly as it reacted with the internal double bonds.

In polyisoprene, the rate constants for the internal and external double bonds are of the order of 100 and 0.5 respectively. Therefore it is a reasonable approximation to say that during the time in which the internal double bonds are almost completely oxidized, only a few per cent of the external bonds have reacted. This means that the second order rate equation with $P - I$ instead of P for the concentration of perbenzoic acid can be used for the reaction of the external double bonds.

For the large values of t for which the approximate equation may be used, practically all of the internal double bonds will have reacted, and the value of X in Equation (1), which is the concentration of external double bonds oxidized, can be found by subtracting I from the total concentration of double bonds oxidized. If R is the fraction of double bonds oxidized, and A is the initial total concentration of double bonds, then $X = RA - I$.

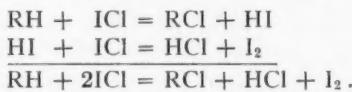
After substituting this value of X in Equation (1), the logarithmic term can be separated into two parts, one of which depends only on measurable quantities, and the second on the composition of the polymer.

$$kt = \frac{1}{(P - I) - E} \quad 2.303 \log \frac{E(P - I - RA + I)}{(P - I)(E - RA + I)}$$

$$\frac{(P - A) kt}{2.303} = \log \frac{P - RA}{A - RA} + \log \frac{A - I}{P - I}. \quad (2)$$

Since R is measured experimentally and A is known, it is possible to plot $\log (P - RA)/(A - RA)$ versus t , and the resulting curve should be a straight line for the values of t for which the approximations made in deriving the equation are valid. By extrapolating the straight part of the curve back to $t = 0$ the term $\log (A - I)/(P - I)$ can be read from the graph, and since A and P are known, the value of I can be calculated. The percentage of vinyl groups in the polymer is then $100(A - I)/A$. For routine work the value of the rate constant can be measured from the slope of the line, and used to construct a calibration curve, as was done by Kolthoff and Lee.

In order to prepare a polymer solution containing a known concentration of double bonds it is necessary to have an accurate method for determining the total unsaturation. Iodine monochloride has been used for this determination (6) but some method of correcting for the amount used in substitution reactions is necessary. The substitution reaction may be represented as:



For each molecule of iodine monochloride used in substitution, one molecule of iodine is formed. Lee, Kolthoff, and Mairs (8) adapted the procedure of Andrews (1) to measure the amount of iodine in the reaction mixture and hence the amount of iodine monochloride used in substitution. In their procedure a sample of the reaction mixture is pipetted into 6*N* hydrochloric acid and the iodine is oxidized to iodine monochloride with standard potassium iodate.

In the present work it was found that the end point depended to a certain extent on the rate at which the sample was shaken during the titration. If the mixture was not shaken at a very rapid rate during the titration the amount of potassium iodate to reach the end point increased.

In order to test for the possibility of oxidation of the hydrochloric acid itself, 10 ml. portions of a standard solution of potassium iodate were pipetted into 50 ml. of 6*N* hydrochloric acid and allowed to stand for various lengths of time. The hydrochloric acid was then neutralized with sodium hydroxide and cooled to room temperature. To test for the amount of oxidizing agent left in the solution, 3 ml. of 2*N* sulphuric acid and 10 ml. of 10% potassium iodide solution were added, and the liberated iodine was titrated with standard sodium thiosulphate. Near the end point, 2 ml. of 1% starch solution was added. The molarity of the potassium iodate was 0.00495 and that of the

sodium thiosulphate was 0.05013 M. Therefore, if none of the oxidizing agent had been used up, the thiosulphate titration should have taken 5.93 ml. The results are shown in Table I.

TABLE I
TEST FOR OXIDATION OF HYDROCHLORIC ACID

| Time (min.) | Volume of $\text{Na}_2\text{S}_2\text{O}_3$ | % of KIO_3 left |
|-------------|---|--------------------------|
| 0.5 | 5.55 | 93.7 |
| 5.0 | 5.31 | 89.6 |
| 10.0 | 5.12 | 86.3 |
| 10.0 | 4.95 | 83.5 |

The samples of polymer were precipitated from the latex with isopropyl alcohol and dried under vacuum. They were purified by dissolving them in benzene, filtering off any gel, and reprecipitating from absolute alcohol. After this purification, the samples were again dried under vacuum for 36 hr., weighed out to make a solution 0.02 M in double bonds, and dissolved in chloroform in volumetric flasks. The solutions were cooled to 0°C., and enough of a benzene solution of perbenzoic acid was added to make the solution 0.03 M. At different intervals of time 20 ml. samples were pipetted into 50 ml. of 0.4 N acetic acid and titrated with standard sodium thiosulphate.

Results of Titrations for Natural Rubber

The volume V of 0.05066 N sodium thiosulphate used in the back titrations is tabulated in Table II. Since the amount of perbenzoic acid used reached a

TABLE II
REACTION OF NATURAL RUBBER WITH PERBENZOIC ACID

| Time (hr.) | V , ml. | R | $\log_e \frac{P - RA}{P(1 - R)}$ | k |
|------------|-----------|--------|----------------------------------|--|
| 1.25 | 9.52 | 0.8974 | 0.5927 | 109.0 liter m. ⁻¹ hr. ⁻¹ |
| 2.08 | 8.56 | 0.9582 | 0.9366 | 103.7 |
| 3.42 | 8.10 | 0.9873 | 1.430 | 96.3 |
| 4.25 | 7.98 | 0.9948 | 1.811 | 98.0 |
| 15.00 | 7.90 | 1.0000 | | |
| 23.42 | 7.89 | 1.0010 | | |
| 27.25 | 7.89 | 1.0010 | | |
| 39.00 | 7.89 | 1.0010 | | |
| 47.00 | 7.89 | 1.0010 | | |

constant value after a relatively short time, it was assumed that no vinyl groups were present. The rate constant for the reaction of internal double bonds was calculated from the ordinary second order rate equation.

$$\begin{aligned} kt &= \frac{1}{P - A} \quad \log_e \frac{A (P - X)}{P (A - X)} \\ &= \frac{1}{P - A} \quad \log_e \frac{(P - RA)}{P (1 - R)} \end{aligned} \quad (3)$$

R = fraction of double bonds oxidized,

A = total initial concentration of double bonds,

P = total initial concentration of perbenzoic acid.

In Fig. 1 the function $\log_e \frac{P - RA}{P (1 - R)}$ is plotted against time.

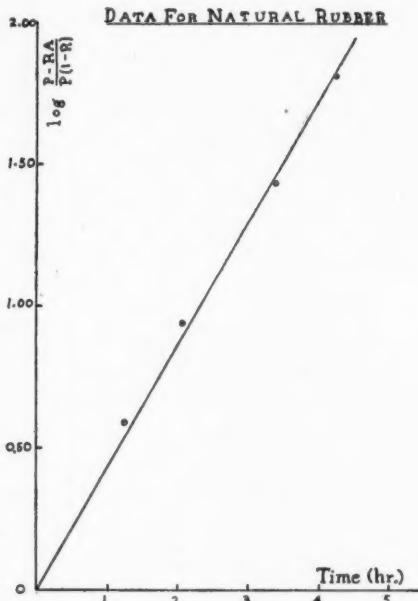


FIG. 1.

The value of the rate constant obtained from this graph is $98.6 \text{ liter m.}^{-1} \text{ hr.}^{-1}$.

Results of Titrations for Synthetic Polyisoprenes

The three synthetic latices were prepared as follows:

- A. 225 ml. N_2O
- 100 gm. Isoprene
- 4.8 gm. R.R.C. soap

0.1 gm. FeSO_4
 0.2 gm. Dodecylmercaptan
 6 ml. 3% H_2O_2
 Polymerization time—24 hr. (2)

- B. 180 ml. H_2O
 100 gm. Isoprene
 4.8 gm. R.R.C. soap
 0.1 gm. FeSO_4
 1.0 gm. $\text{Na}_2\text{P}_2\text{O}_7$
 0.2 gm. M.T.M.-4 (mixed tertiary mercaptans)
 0.2 gm. Cumene hydroperoxide
 1.0 gm. Glucose
 Polymerization time—2.5 hr. (12)
- C. 200 ml. H_2O
 100 gm. Isoprene
 4.5 gm. R.R.C. soap
 0.8 gm. *p*-Tolyl diazo- β -naphthyl thioether
 Polymerization time—16 hr. (12)

In each case the polymerization was carried out at 45°C.

Two samples of Polymer A, and one each of B and C were analyzed.

The results are tabulated in Tables III, IV, V, VI.

TABLE III
 REACTION OF POLYMER A (SAMPLE 1) WITH PERBENZOIC ACID

| <i>t</i> (hr.) | <i>V</i> | <i>R</i> | <i>RA</i> | $\log \frac{P - RA}{A - RA}$ |
|----------------|----------|----------|-----------|------------------------------|
| 0.25 | 14.22 | 0.5997 | 0.01199 | |
| 0.75 | 12.57 | 0.8069 | 0.01614 | |
| 1.33 | 10.39 | 0.8423 | 0.01685 | |
| 2.75 | 9.83 | 0.8780 | 0.01756 | |
| 4.83 | 9.66 | 0.8885 | 0.01777 | 0.7391 |
| 5.42 | 9.65 | 0.8891 | 0.01778 | 0.7411 |
| 7.00 | 9.61 | 0.8917 | 0.01783 | 0.7496 |
| 8.50 | 9.59 | 0.8930 | 0.01786 | 0.7538 |
| 10.00 | 9.57 | 0.8942 | 0.01788 | 0.7580 |
| 12.08 | 9.57 | 0.8942 | 0.01788 | 0.7580 |
| 21.25 | 9.46 | 0.9012 | 0.01802 | 0.7827 |
| 24.83 | 9.44 | 0.9025 | 0.01805 | 0.7874 |
| 26.00 | 9.42 | 0.9037 | 0.01807 | 0.7920 |
| 31.00 | 9.36 | 0.9075 | 0.01815 | 0.8066 |
| 47.42 | 9.22 | 0.9165 | 0.01733 | 0.8443 |

The function $\log \frac{P - RA}{A - RA}$ is plotted against *t* for Polymers A, B, and C in

Figs. 2, 3, and 4 respectively. The percentages of vinyl groups and the rate constants for the vinyl groups are calculated from these graphs and are shown in Table VII.

TABLE IV
REACTION OF POLYMER A (SAMPLE 2) WITH PERBENZOIC ACID

| <i>t</i> (hr.) | <i>V</i> | <i>R</i> | <i>RA</i> | $\log \frac{P - RA}{A - RA}$ |
|----------------|----------|----------|-----------|------------------------------|
| 0.50 | 11.94 | 0.7442 | 0.01488 | |
| 1.58 | 10.22 | 0.8531 | 0.01706 | |
| 3.42 | 9.73 | 0.8842 | 0.01768 | 0.7250 |
| 4.75 | 9.64 | 0.8898 | 0.01780 | 0.7432 |
| 6.83 | 9.62 | 0.8910 | 0.01782 | 0.7472 |
| 12.16 | 9.56 | 0.8949 | 0.01790 | 0.7602 |
| 14.00 | 9.55 | 0.8955 | 0.01791 | 0.7622 |
| 21.25 | 9.45 | 0.9018 | 0.01804 | 0.7846 |
| 26.00 | 9.41 | 0.9044 | 0.01809 | 0.7944 |
| 34.00 | 9.36 | 0.9075 | 0.01815 | 0.8066 |
| 50.00 | 9.20 | 0.9178 | 0.01836 | 0.8500 |

TABLE V
REACTION OF POLYMER B WITH PERBENZOIC ACID

| <i>t</i> (hr.) | <i>V</i> | <i>R</i> | <i>RA</i> | $\log \frac{P - RA}{A - RA}$ |
|----------------|----------|----------|-----------|------------------------------|
| 0.92 | 11.41 | 0.7774 | 0.01555 | |
| 1.83 | 10.51 | 0.8347 | 0.01669 | |
| 3.17 | 10.26 | 0.8505 | 0.01701 | |
| 4.08 | 10.18 | 0.8556 | 0.01711 | 0.6497 |
| 14.68 | 9.99 | 0.8676 | 0.01735 | 0.6792 |
| 23.08 | 9.88 | 0.8746 | 0.01749 | 0.6980 |
| 27.08 | 9.86 | 0.8759 | 0.01752 | 0.7015 |
| 38.67 | 9.79 | 0.8803 | 0.01761 | 0.7140 |
| 47.00 | 9.71 | 0.8854 | 0.01771 | 0.7293 |

TABLE VI
REACTION OF POLYMER C WITH PERBENZOIC ACID

| <i>t</i> (hr.) | <i>V</i> | <i>R</i> | <i>RA</i> | $\log \frac{P - RA}{A - RA}$ |
|----------------|----------|----------|-----------|------------------------------|
| 1.08 | 10.68 | 0.8239 | 0.01648 | |
| 2.00 | 9.97 | 0.8689 | 0.01738 | |
| 3.25 | 9.66 | 0.8885 | 0.01777 | |
| 4.17 | 9.60 | 0.8923 | 0.01785 | 0.7515 |
| 14.83 | 9.42 | 0.9037 | 0.01807 | 0.7919 |
| 23.42 | 9.33 | 0.9005 | 0.01819 | 0.8146 |
| 27.17 | 9.29 | 0.9120 | 0.01824 | p. 8249 |
| 38.83 | 9.20 | 0.9178 | 0.01836 | 0.8502 |
| 47.08 | 9.14 | 0.9214 | 0.01843 | 0.8669 |

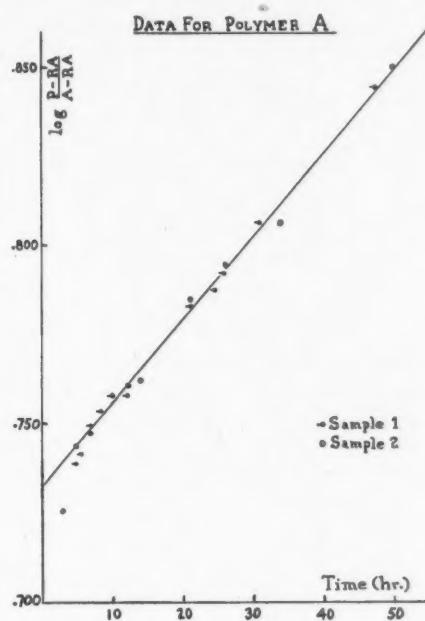


FIG. 2.

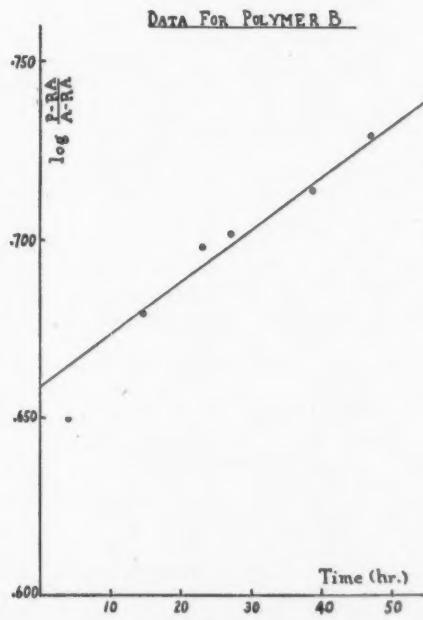


FIG. 3.

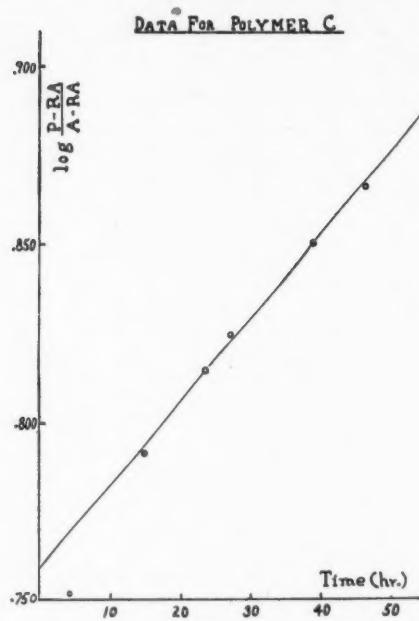


FIG. 4.

TABLE VII
RATE CONSTANTS FOR VINYL GROUPS AND PERCENTAGE OF
VINYL GROUPS FOR POLYMERS A, B, AND C

| Catalyst system | k (liter m. ⁻¹ hr. ⁻¹) | % of vinyl groups |
|---|---|-------------------|
| A. $H_2O_2\text{-FeSO}_4$ | 0.535 | 11.5 |
| B. Cumene hydroperoxide | 0.337 | 14.0 |
| C. p -Tolylidazo- β -naphthyl thioether | 0.530 | 10.5 |

The rate constants k_I for the reaction of the internal double bonds were calculated from data obtained in the first three hours of the reactions, by neglecting the reaction of the external double bonds in this time. See Tables VIII, IX, X.

TABLE VIII
DATA FOR CALCULATION OF k_I FOR POLYMER A

| t (hr.) | RA | $\log_e \frac{I}{P} (P - RA)$ | k_I liter m. ⁻¹ hr. ⁻¹ |
|-----------|---------|-------------------------------|--|
| 0.25 | 0.01199 | 0.62 | 202 |
| 0.50* | 0.01488 | 1.15 | 187 |
| 0.75 | 0.01614 | 1.66 | 180 |
| 1.33 | 0.01685 | 2.21 | 135 |
| 1.58* | 0.01756 | 2.48 | 128 |
| 2.75 | 0.01736 | 3.96 | 117 |

TABLE IX
DATA FOR CALCULATIONS OF k_I FOR POLYMER B

| t (hr.) | AR | $\log_e \frac{I (P - RA)}{P (I - RA)}$ | k_I liter m. ⁻¹ hr. ⁻¹ |
|-----------|---------|--|--|
| 0.92 | 0.01555 | 1.61 | 137.0 |
| 1.83 | 0.01669 | 2.71 | 116.0 |
| 3.17 | 0.01701 | 3.67 | 90.4 |

TABLE X
DATE FOR CALCULATION OF k_I FOR POLYMER C

| t (hr.) | AR | $\log_e \frac{I (P - AR)}{P (I - AR)}$ | k_I liter m. ⁻¹ hr. ⁻¹ |
|-----------|---------|--|--|
| 1.08 | 0.01648 | 1.74 | 133 |
| 2.00 | 0.01738 | 2.67 | 110 |
| 3.25 | 0.01777 | 4.03 | 102 |

The equation used to calculate k_I is:

$$k_I t = \frac{1}{P - I} \quad \log_e \frac{I (P - RA)}{P (I - RA)} \quad (6)$$

RA = concentration of double bonds oxidized in time t ,

I = initial concentration of internal double bonds,

P = initial concentration of perbenzoic acid.

The two values of t marked thus * in Table VII are for Sample 2, and the remainder are for Sample 1.

Conclusions

Figs. 2, 3, and 4 indicate that the extrapolation of the plot of $\log (P - RA)/A (1 - R)$ is probably in error by less than 0.005. An error of this size in the value of $\log \frac{P - I}{A - I}$ would make an error in the calculated percentage of

v vinyl groups of about 2 parts in 1000. Probably the uncertainty in the percentage of vinyl groups due to errors in the titrations and in the extrapolation is not more than 0.2 %. The principal advantages of this method of calculation are: (1) no approximate estimate of I from the rate curve is necessary, and (2) the graph tends to cancel errors in any single titration.

There is an error due to the assumption that the polymers are 100% unsaturated, but it seems to be unavoidable, and for polymers of similar types the error would probably be the same for each.

The rate constants for the reaction of the vinyl groups in Polymers A and C with perbenzoic acid are almost the same, but they are about 60% greater than that for Polymer B. Furthermore, the points in Fig. 3 (Polymer B) do not fall as close to a straight line as they do in Figs. 2 and 4.

These facts suggest that the vinyl groups in Polymers A and C differ from some of those in Polymer B: perhaps B contains a mixture of two kinds of vinyl groups. The only possible kinds of vinyl groups are those formed by 1-2 or 3-4 addition and the 3-4 addition product would be expected to be the faster reacting because of its extra methyl group on the ethylene.

The catalyst system used for the polymerization has a small effect on the amount of vinyl groups, but the most interesting difference between the three polymers is the possibility that B contains 1-2 and 3-4 units, while A and C contain only 3-4 units in appreciable quantities. Polymer B also differs markedly from A and C in the speed of the polymerization.

The values of the rate constants for the internal double bonds decrease with time, as shown by tables VIII, IX and X. There are two possible explanations for this decrease.

1. The formation of the epoxide on the first internal double bonds to react decreases the rate of the reaction of the remaining double bonds. It is known that negative groups close to the ethylene slow down the rate of addition of perbenzoic acid; but the epoxide would be at least three carbon atoms away from any unreacted ethylenes, and the effect would not likely be as great as is observed with Samples A, B, and C.

2. There may be two kinds of internal double bonds present that react with perbenzoic acid at different rates. Since only 1-4 addition leads to internal double bonds, the two kinds would have to be those due to *cis*, 1-4 and *trans*, 1-4 addition.

Natural rubber is known to be almost completely *cis*, 1-4 polyisoprene. From Fig. 2 the rate constant for the reaction of the double bonds with perbenzoic acid is 98.6 liter m.⁻¹ hr.⁻¹. In natural rubber the small decrease with time is not nearly as great as that observed with the synthetic polymers. The observed rate constant for natural rubber is within 10% of 100 liter m.⁻¹ hr.⁻¹ for the complete reaction, but for the synthetic polymers the rate constant decreases from about 200 liter m.⁻¹ hr.⁻¹ at the start of the reaction to about 100 liter m.⁻¹ hr.⁻¹ after three hours.

Probably the small decrease of the rate constant for natural rubber is due to the inductive effect of the epoxide groups: the larger decrease in the synthetic polymers presumably is due partly to this, but largely to the presence of *cis* and *trans* isomers in the 1-4 addition units.

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AN INTERFEROMETER FOR THE THICKNESS MEASUREMENT OF THIN TRANSPARENT FILM¹

BY N. SIDJAK*

Abstract

A compact interferometer for rapid measurement of the thickness of thin transparent films is described. The measurement involves only the counting of the dark interference bands in a continuous spectrum. It has a range of 1 to 50μ and an accuracy of measurement of approximately 2%. It is particularly suited to the measurement of mica and other thin transparent materials used for windows on counters and apparatus employed in work on radioactive substances. Windows already mounted in recessed holders can be readily measured. Details of the construction and design of the instrument are given.

Introduction

Counters and other apparatus used in connection with radioactive substances employ windows consisting of thin films of low density materials to allow the passage of alpha and beta particles. In many cases the thickness of the film or its mass per unit area must be known accurately. Mechanical methods of measurement are not satisfactory for very thin films. Weighing is tedious and not always convenient. Optical methods are to be preferred and the instrument described employs the principle of interference to produce a banded spectrum from which the measurement can be made. It was designed especially for the measurement of thin mica sheets, but can be used equally well for other transparent materials. Similar instruments have previously been mentioned or described in rather less detail (1, 2).

Theory of Operation

When light is reflected from a thin transparent plate or film along a fixed direction, the first reflected rays of certain wave lengths are cancelled by interference from subsequent reflections. At the positions in the continuous spectrum corresponding to these certain wave lengths there appear dark bands. In Fig. 1 the relative intensities of the rays involved are approximately represented by the various widths of line.

The wave length λ for a dark band is such that if t = the thickness of the film, r = the angle which the internal ray makes with the normal to the film and μ = the refractive index at wave length λ

$$m\lambda = 2t\mu \cos r$$

when m is an integer.

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* On August 7, 1950, N. Sidjak lost his life in a drowning accident.

For dark bands at λ_1 and λ_2 there is an integral number of bright intervals between them which is given by

$$n = m_2 - m_1 = 2t \cos r \left(\frac{\mu_2}{\lambda_2} - \frac{\mu_1}{\lambda_1} \right) \dots \dots \dots (1)$$

that is, the thickness of the film is proportional to the number n if $\lambda_1, \lambda_2, \mu_1, \mu_2$, and r are fixed, which is the case in the present instrument; λ_1 and λ_2 are chosen to lie in the spectrum as far apart as is consistent with good visibility. Approximate values are 6500 Å and 5000 Å. In use n is determined as accurately as possible to the nearest fractional part.

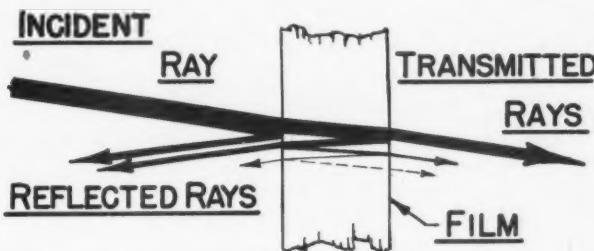


FIG. 1. *Interference in thin film.*

In dealing with windows for radiation counters it is usual to express the thickness in terms of area density, i.e.,

$$t = W/\rho \times 10^3$$

when W = area density in mgm./cm.², and ρ density in gm./cm.³. Hence, putting $\mu_1 = \mu_2 = \mu$ and λ in A .

$$W = n \left[\frac{\rho}{2 \mu \cos r} \left(\frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} \right) \right] 10^{-5} \dots \dots \dots (2)$$

Taking $\mu = 1.58$, $r = 7^\circ$, $\lambda_1 = 6500$, $\lambda_2 = 5000$, $\rho = 2.85$, we obtain $W = 0.197 n$ for mica.

In practice, owing to uncertainties in all the constants in expression (2), it is better to calibrate the instrument with standard films of known thickness. For convenience λ_1 and λ_2 are chosen, as will be discussed later, such that

$$W = 0.200n \text{ for mica.}$$

For materials other than mica the calibration must be corrected by the factor

$$\left(\frac{\rho}{\mu} \right)_{\text{sample}} / \left(\frac{\rho}{\mu} \right)_{\text{mica.}}$$

To produce a bright pattern in the field of view, an intense beam of light is required and all of this light must strike the film nearly in one direction so that a dark fringe corresponding to one wave length is not illuminated by light of

the same wave length reflected from the film at a different angle of incidence where destructive interference does not occur. It is best to use an angle of incidence as close to the normal as possible where a slight change of angle does not change the path length appreciably.

Instrument Design

General Optical System

As shown in Fig. 2, an intense parallel beam of light from a collimator strikes the film being measured, from which part of it is reflected. The reflected beam

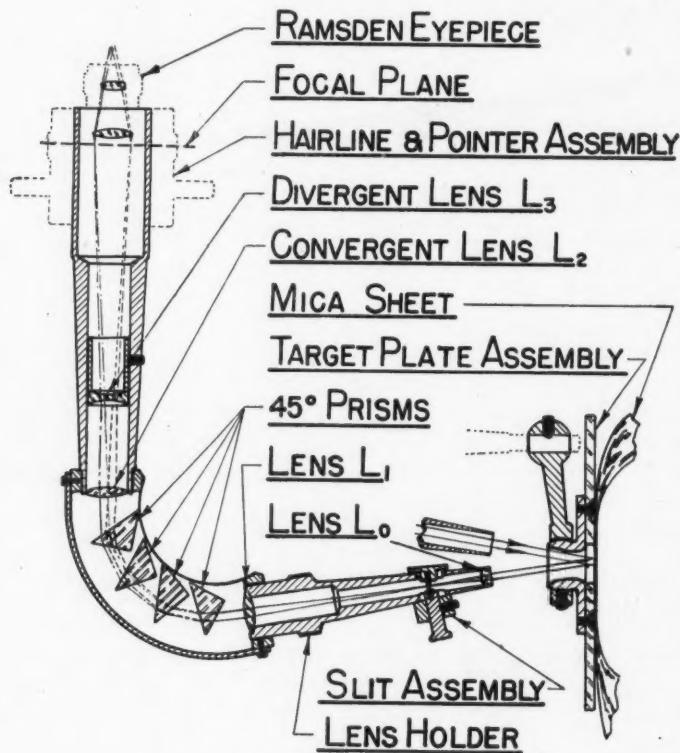


FIG. 2. Spectroscopic assembly.

is focussed by a small lens L_0 on to the slit of a spectroscope. The banded continuous spectrum is viewed through the eyepiece of the spectroscope telescope. The number of dark bands seen between two hairlines in the focal plane of the eyepiece is a measure of the thickness of the film. To facilitate counting of the number of bands a pointer is provided which can be traversed slowly between the hairlines by a simple manual control.

The Spectroscope

Four prisms in series (Fig. 2) provide for the dispersion in the spectroscope and allow for a "wrap around" arrangement of components. Further compactness is achieved by introduction of a diverging lens L_3 into the telescope tube. In this particular case the distance between L_2 and the focal plane of the eyepiece is $2/3$ of that which would have been required to produce the same magnification had the diverging lens been omitted. This lens also facilitates the preset focussing adjustment of the instrument.

During the design and construction of the instrument, achromatic lenses were not used because of the experimental nature of the work, and since completion, there has been no need to convert.

The Collimator

The arrangement of the light source and collimator shown in Fig. 3 was dictated mainly by practical considerations to achieve a compact and con-

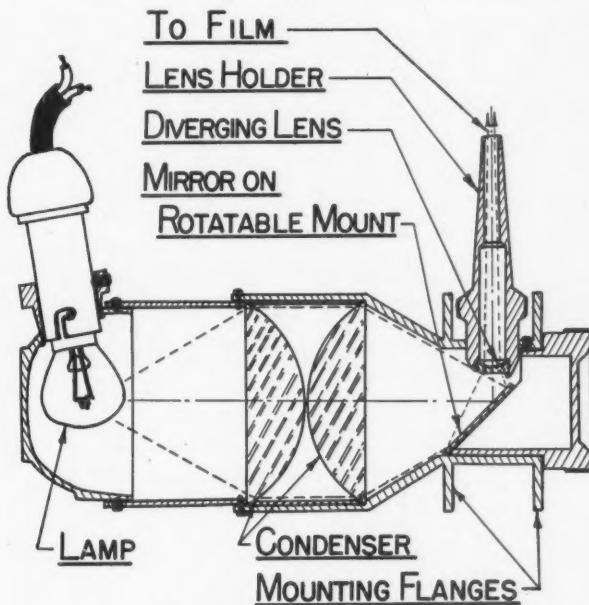


FIG. 3. *Collimator assembly.*

venient assembly. In particular it was required to mount close to the spectroscope assembly as shown in Fig. 2. The convergence of the beam is controlled by moving the lamp closer to or farther away from the condensing lenses. The direction of the beam is controlled by moving the lamp along its central axis in conjunction with rotation of the mirror. This mirror serves also to change the direction of the beam through 90° which assists in making the whole instrument compact.

The target plate (see Fig. 2) against which the film is placed for measurement is mounted on a ball-and-socket joint which can itself be moved in three dimensions. This allows complete freedom for adjustment during setting up. The target plate assembly is pivoted so that it will swing out of the way upwards to permit measurements of films already mounted in recessed holders.

The Hairline and Pointer Assembly

The hairlines consist of fine wires attached to spring clips which are held fixed by friction in two slots in a movable carrier. The counting pointer is mounted on another carrier. A view of the positions of the hairlines and the counting pointer with respect to a sample banded spectrum is shown in Fig. 4.

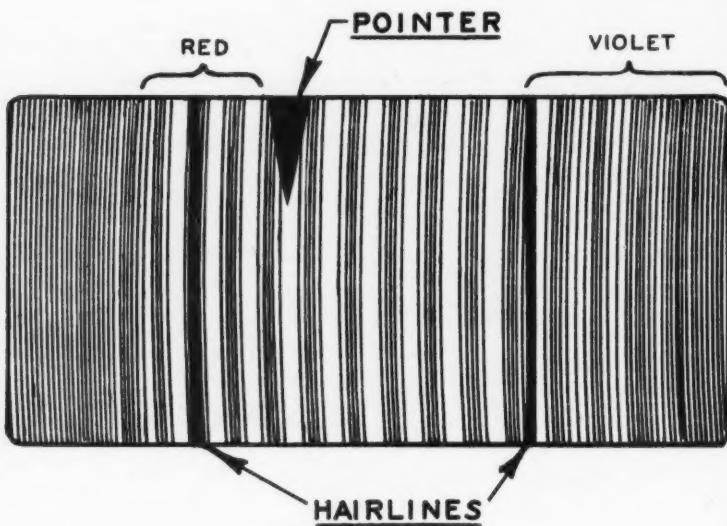


FIG. 4. *Field of view.*

Movement of both carriers is controlled by means of rings provided with eccentric races (Fig. 5). Only slight movement of the hairlines is required, and only in the initial calibration merely to locate one of them on the center of a dark band. A much larger range of movement is necessary in the case of the pointer. With reference to Fig. 6, where the full and dotted lines show two positions of the slide and eccentric, it can be seen that a circular eccentric would not operate without a very large amount of backlash because the length CD is much larger than that of the slide which can only be of length AB. A noncircular race, also seen in Fig. 6, composed of the segments of two circles such that $A'B' = C'D'$, was therefore used in the instrument.

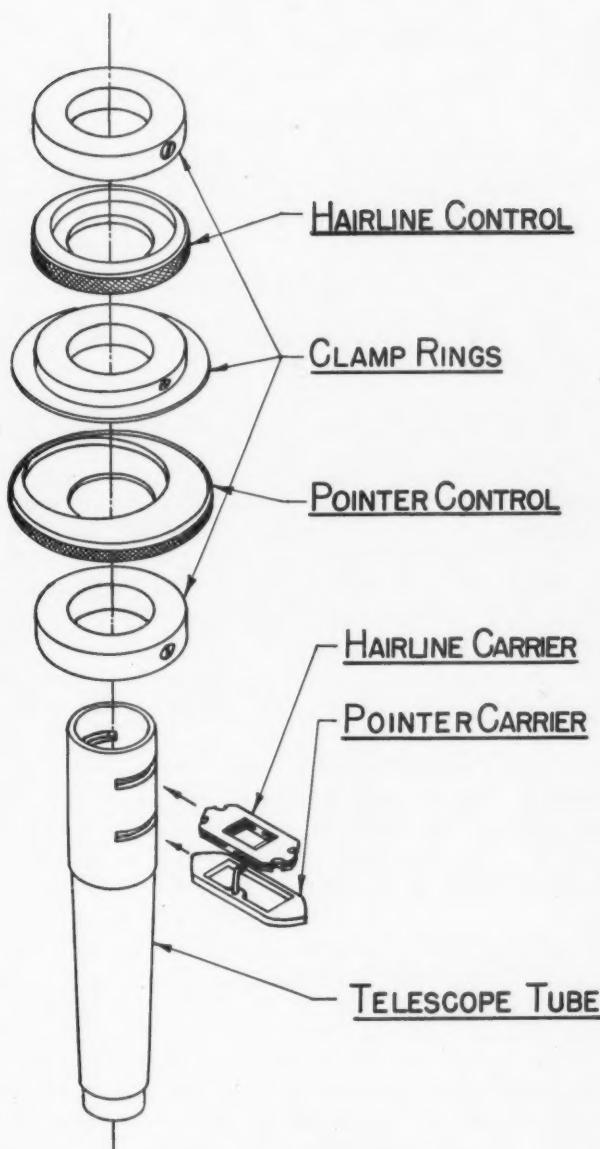


FIG. 5. Hairline and pointer assembly.

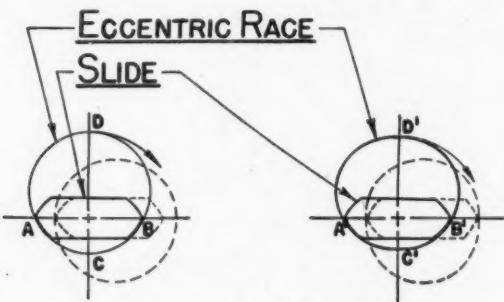


FIG. 6. Eccentric for pointer movement.

Hairline Adjustment

It was clearly desirable in practice to have a simple relationship between the number of bands observed and the area density in mgm./cm.² for mica. As shown earlier a calculation suggested that 0.2 would be a suitable constant of proportionality in expression (2).

A number of uniform sheets of mica covering the desired range of the instrument were weighed accurately and the areas measured. Using these as standards the hairlines were adjusted so that $W = 0.200 n$, e.g. 8.4 band intervals (Fig. 4) represent a "thickness" of $0.2 \times 8.4 = 1.68$ mgm./cm.². A further check on the adjustment was obtained by mechanical measurement of thicker sheets on a sensitive gauge instrument.

After setting up and calibrating, all adjustments affecting the hairline position were locked to prevent inadvertent changes during use.

Range and Accuracy

The lower limit to the measurable thickness has not been reached, but would be of the order of one band interval, or 0.2 mgm./cm.², which is equivalent to about $3/4\mu$. The upper limit appears to be about 60 bands, or 12 mgm./cm.², which is equivalent to about 50μ . Counter windows in general fall well within this range.

Accuracy is limited by the user's ability to approximate the decimal location of a hairline in a band interval. When a large number of bands (about 50) fill the field, the hairlines can be read to the nearest half interval. When only a small number of bands (about 5-15) are present, the hairlines can be read to better than 1/10th of an interval, which gives the same percentage accuracy of about 2%. With fewer than five bands the percentage accuracy is rather less. With some experience, measurements to the above-mentioned accuracy of 2% are obtainable over most of the range. Careless placement of the mica against the target plate results less in band displacement than in poorer definition. In effect, the band pattern disappears before it can give an erroneous result.

General Considerations

The assembled instrument (Fig. 7) stands $7\frac{1}{2}$ in. high on a pedestal $4\frac{3}{4}$ in. $\times 5\frac{1}{2}$ in. Other variations of the arrangement of components could be used. For instance, the target plate could be located at the left of the telescope instead of as shown, or the components completely rearranged to allow for

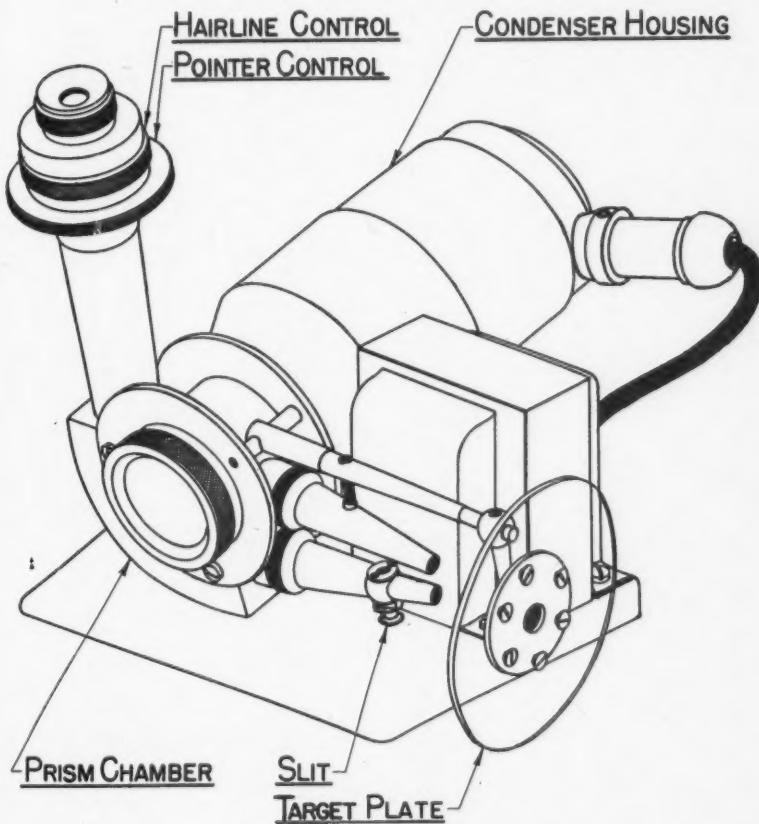


FIG. 7. Complete interferometer.

laying the mica on a horizontal table. The instrument could also be constructed with fewer adjustments, once the required fixed positions have been determined. The instrument has proved much more satisfactory than any mechanical method of measurement and has the great advantage over the latter in that windows already assembled on completed counters can be measured and it is not subject to errors occasioned by dust particles, etc. From the operator's point of view it is quick and easy to use.

Acknowledgment

The writer wishes to thank Mr. I. L. Fowler of the Counter Development Section for pointing out the need for such an instrument as described in this paper, also for his numerous helpful suggestions during the design and construction of the instrument, and for his guidance during preparation of this report.

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NOTE

A New Method for Moisture Determination in Soil

It is well known that a mixture of radium and beryllium emits neutrons and that neutrons from such a source can be used to activate a metal such as indium, $In^{115} + n \rightarrow In^{116}$. The In^{116} is radioactive and emits a beta particle, the half life of the In^{116} being 54 min. (2). It is also known that indium exhibits a large "water effect". Thus, a piece of indium foil left in a test tube with a 250 mc. Ra-Be neutron source for 15 min. acquires an activity of 320 counts per minute. When the test tube and contents are surrounded by paraffin wax, the activity acquired under the same conditions is 15,000 counts per minute. This is due to the fact that the fast neutrons emitted by the Ra-Be neutron source are slowed down and scattered by the hydrogenous material, and are then more readily absorbed by the indium, partly owing to the higher absorption cross section at lower energies and partly owing to the slow neutrons staying around longer, rather like a swarm of bees. The absorption cross section for slow neutrons (0.025 ev.) is 200 barns and for fast neutrons (1 mev.) is 0.1 barns (1).

The effect of an hydrogenous medium on neutron distribution is made use of in neutron well-logging.

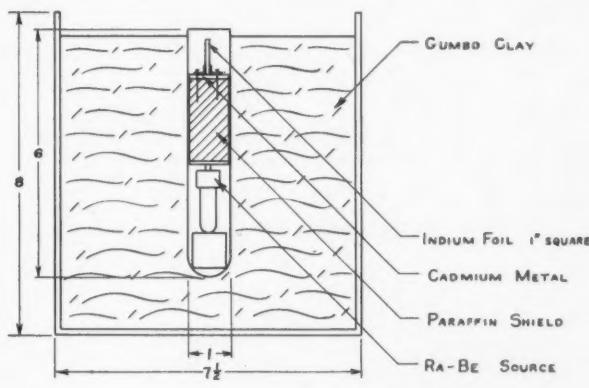


FIG. 1. Initial apparatus.

The foregoing facts led the authors to investigate the possibility of using neutron scattering to measure soil moisture. The apparatus used in preliminary experiments last fall* is shown in Fig. 1. A 250 mc. Ra-Be neutron source was

* Reported at the Annual Meeting of the Associate Committee on Soil and Snow Mechanics of the National Research Council in December 1950. At this meeting our attention was drawn to a report of similar experiments by American workers.

separated from a square of indium foil by a small plug of paraffin capped with a piece of cadmium metal, the cadmium foil serving to prevent the direct access of slow neutrons to the indium foil. The whole arrangement was placed in a test tube, mounted vertically in a beaker of gumbo clay. The indium foil was activated for 70 min. and then counted after a fixed time under a thin window Geiger counter connected to a scaler (scale of 64) and register. The results obtained for different percentages of moisture are shown in Fig. 2. They indicate that the induced radioactivity shows a strong dependence on the moisture content of the soil. Since then, the improved arrangement, shown in Fig. 3, has been used. Using a 4-in. square of indium foil, irradiation time was cut down to five minutes. The activity of the foil was measured by slipping it over a

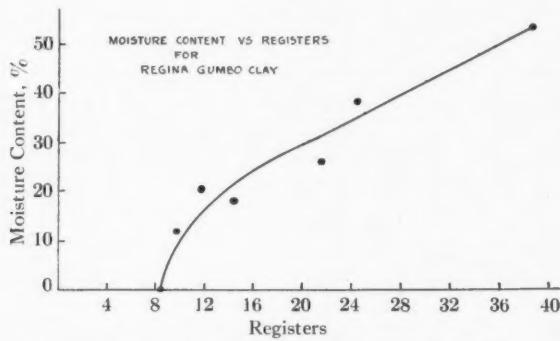


FIG. 2. *Induced radioactivity (registers per minute) versus moisture content.*

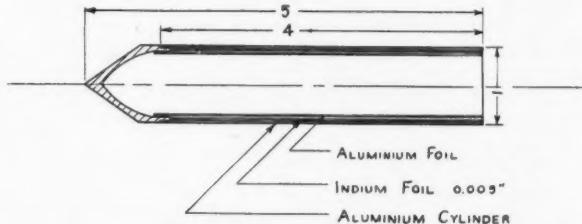


FIG. 3. *Improved apparatus for determining moisture content of soil.*

Thyrode 1B85 counter tube. The results obtained (Fig. 4 (a)) confirm the results of the preliminary experiments and indicate that with a larger foil a shorter time of irradiation is adequate and that actually a much smaller Ra-Be source could have been used.

Readings were also taken by placing the foil in its aluminum housing around the Geiger tube of a portable beta-gamma rate meter (Nuclear Instrument Co. Type 2610A). The scale readings show the same dependence on moisture

content (Fig. 4(b)). The fact that one can get good readings using a portable counter is important since one might often wish to make the soil moisture readings away from a power supply. In the field, for example, in examining

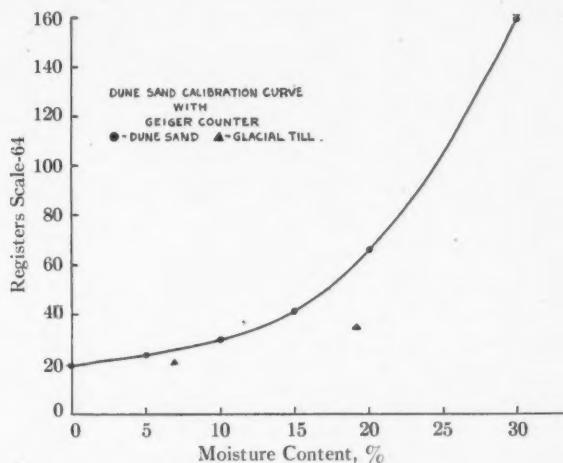


FIG. 4 (a). Induced radioactivity versus moisture content, radioactivity measured using scale of 64 scaler.

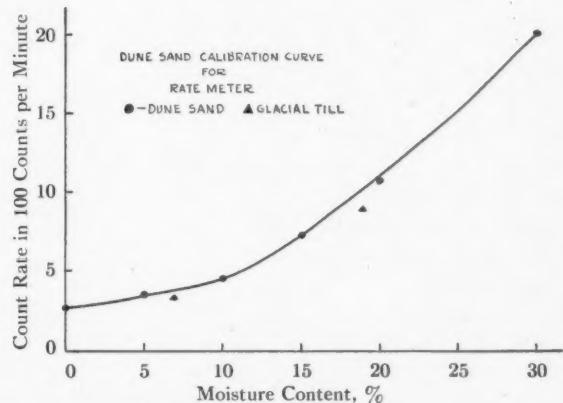


FIG. 4 (b). Induced radioactivity versus moisture content, radioactivity measured using rate meter.

the moisture content of a road subgrade, an aluminum tube would be driven into the ground to the desired depth and the moisture content of the soil determined at various levels by mounting the foil and source at various levels (the foil gives an average value for the soil within about a 4 to 6 in. radius of it).

While a good deal more development work will have to be done, the method was felt to be of sufficient promise to report in this preliminary form at the present time.

Financial assistance from the Saskatchewan Research Council is gratefully acknowledged.

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